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Novel state-of-the-art computational techniques were developed and validated for studying collisional processes responsible for producing infrared and ultraviolet signatures in rocket plumes. The promising new methods involve computation of cross sections and rates within a semiclassical methodology. Two of the key beneficiary programs within the USAF are the SPURC and the CHARM programs which require detailed microscopic dynamical information (kinetic rates and cross sections) about such collisional processes for successful modeling of the chemistry within appropriate flowfield simulation codes.

Successful prediction and interpretation of ultraviolet signatures require treating collision induced transitions between different electronic states caused by the coupling between electronic and nuclear motions in molecules during collisions. Electronic transitions bring in inherently quantum mechanical effects that have no analog in classical mechanics. The task of numerically solving the quantum mechanical equations of motion is still an unsolvable computational problem for many realistic molecular systems. The semiclassical theory is accurate enough to reproduce specific quantum mechanical features *necessary* absent in the classical picture and computationally practical because it leads to ordinary differential equations instead of the partial differential equations of quantum mechanics.

Electronic structure information required in modelling the production of candidate excited species, nitrogen, nitric oxide, and hydroxyl radical molecules in some elementary reactions was analyzed. It was determined that modern quantum chemistry can provide all the required information involving excited hydroxyl production and less extensive data for other systems. *(jhd)*

Introduction

One critical area of military technology that is relevant to both the Air Force and the Strategic Defense Initiative (SDI) is the requirement to locate ballistic missiles, particularly during the boost phase of the trajectory. To this end, codes that model radiation emitted from rocket plumes have been developed over a number of years extending back to the sixties. With the advent of SDI, the requirements on these codes have been made more stringent, and the precision required in their predictions has increased, in large part due to the need to pinpoint the hard body within the extended radiation field of the plume.

The need for kinetic data to describe high-altitude phenomena leading to plume signatures has been evident for some time.[1] Since the primary atmospheric components at altitudes of interest are N_2 and $O(^3P)$, cross sections involving these species with exhaust molecules are of particular importance. However, experimental results for processes involving these species have been very difficult to obtain.[2] Because experimental data for a great many of the processes of interest at high altitudes are simply lacking, reliable theoretical data have become essential for the predictive capabilities of plume modelling codes such as CHARM and SPURC.

Theoretical methods are applicable to a wide variety of molecular systems over large velocity ranges. Thus they provide a means to obtain much of the required data; primarily excitation cross sections and rates for vibrational, rotational and electronic energy transfer processes (T-VRE) and for chemical reactions. The purpose of this research was to develop new semiclassical methods to improve the ability of theoretical methods to predict kinetic data of sufficient accuracy to be of use in high-altitude plume technology. Virtually all of the theoretical results for excitation (T-VR) processes of interest in high altitude plume kinetics (i.e. vibrational and rotational excitation of molecules by oxygen atoms) have been provided by the Chemical Dynamics group and their collaborators from research dating back to the late seventies.[3,4] This research was carried out under sponsorship of the Air Force Astronautics Laboratory (AFAL - previously AFRPL). The results covered a number of systems, including H_2O, CO_2, HF, HCl, and CO. The theoretical results significantly extended the data base of available vibrational excitation cross sections and provided a fairly reliable picture of the relative magnitudes of the cross sections. However, of necessity at that time, classical mechanics was used for the dynamical cross section calculations. The need for methods to more accurately treat vibrational energy transfer processes was evident, and with the recent interest in UV signature phenomena, a method applicable to electronic excitation was also needed.

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Successful prediction and interpretation of UV-signatures requires detailed microscopic information about the responsible collisional processes. One of the central processes in this connection is collision-induced transitions between different electronic states. The standard quantum-mechanical description of collisional processes is based on the adiabatic separation of nuclear and electronic motions, assuming that the electrons instantaneously adjust to nuclear motions because of the large difference in their masses. Encounters taking place on a single adiabatic surface can be described in the zeroth-order approximation simply by the classical equations of motion. However transitions from one electronic surface to another are essentially quantum-mechanical processes which have no analogs in classical mechanics. The task of numerically solving the Schroedinger equation governing the collisional processes in question is still an unsolvable computational problem for realistic molecular systems.

Semiclassical theory fills the gap between the quantum and classical treatments. Approximating the quantum mechanical wavefunction by the first term of an asymptotic expansion leads to ordinary first-order differential equations for the semiclassical solutions rather than the more difficult partial differential equations encountered in quantum mechanics. This approximation is valid except for the lowest energies and is sufficiently accurate to reproduce specific quantum-mechanical features which are completely absent in the classical picture. In particular the semiclassical theory is capable of describing the electronically nonadiabatic transitions which are the main concern in the present research.

There is however an essential obstacle that has been hindering progress in this area for many years. At classical turning points the kinetic energy goes to zero and the semiclassical solutions are singular. In one-dimensional problems this situation is corrected using connection formulae.[5] that give the recipe of how to continue the semiclassical wavefunction after its reflection at the turning point. This correction exploits conservation of the flux to connect the incoming and outgoing solutions but is insufficient in the multi-dimensional case as there may be exchange of flux between different degrees of freedom. The current state-of-the-art theory in this area is mainly developed at the level of formal theorems which prove existence of solutions, but do not provide any practical numerical algorithms to find them.

Objectives

The objectives of Phase I were (1) to identify relevant electronic structure input for UV-signature-producing collisional processes involving excited NO, OH and N_2

molecules, and (2) to develop semiclassical techniques capable to provide the necessary state-to-state dynamical information for collisional processes relevant to SPURC.

Task 1 involves examining the molecular correlation diagrams for collisional processes between relevant atmospheric/plume species in order to identify the associated quantum chemical potential energy surfaces and electronic couplings, operative in the energy range of interest. Task 2 involves theoretical developments that enable semiclassical wavefunction computations for multidimensional electronically inelastic systems.

Status of Research

Significant progress on both the tasks of Phase I is reported by presenting detailed results. Most notably, task 2 has resulted in a significant progress in overcoming two most serious problems of the nonadiabatic semiclassical theory, making possible its practical implementation for the quantitative description of processes leading to UV radiation. In addition, an improved method of treating T-V excitation on a single adiabatic surface was also developed.

The adiabatic separation of nuclear motions in the semiclassical picture made it possible to connect incoming and outgoing semiclassical solutions, reproducing correctly interference effects between different trajectories. Validity of the adiabatic separation of streamline and vibrational motions was demonstrated by comparing the semiclassical and exact quantum-mechanical results for vibrational energy transfer in an atom-diatom collision in the IOS approximation[6].

Including the adiabatic hypothesis into the Self-Consistent Eikonal Method (SCEM)[7] gave us a practical tool for treating electronically inelastic processes with a few degree of freedom. As another test of applicability of the single average potential (the so-called Ehrenfest potential obtained by weighting the adiabatic potential functions with the probabilities for the system to be in the appropriate electronic state) we studied vibrational excitation of the diatomic molecule in an atom-diatom collision in the IOS approximation by expanding the Schroedinger equation in the vibrational basis set.

Phase I also resulted in the development of a new extended approach called SCACEM (Self-Consistent Adiabatically-Corrected Eikonal Method) for a more accurate treatment of electronic inelasticity in molecular collisions; this goes beyond the Ehrenfest effective potential approximation employed in SCEM without compromising on the advantages of the latter method. The following executive summary emphasizes the relevant

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implications of our computational approach for future SPURC-related investigations. Phase I results are overviewed in a following section. Two manuscripts (one on the extended formal theory and one on numerical studies) are included as appendices in this report.

Executive Summary

An analysis of the correlation diagrams for dominant collisional pathways leading to excited states of the three candidate molecules (NO, OH, and N_2) was conducted to identify a feasible system for quantum chemistry input. The problem of $OH(^2\Sigma^+)$ radical formation in the reactive process:

$$O(^3P) + H_2 \rightarrow OH(^2\Sigma^+) + H(^2S) \qquad (A)$$
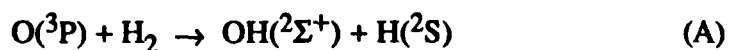
emerges as an immediately feasible case for quantum chemical characterization of potential energy surfaces and interelectronic state couplings. Clearly, the dynamical treatment of process (A) requires a computational description of electronic nonadiabaticity as well as reaction (nuclear rearrangement) leading to an electronically excited $OH(^2\Sigma^+)$ product during collisions.

In Phase I we successfully overcame the most serious principal defect of the semiclassical theory caused by its break-down at classical turning points. We developed a **new technique to construct semiclassical wavefunctions for realistic potential surfaces regardless of the complexity of the latter.** For electronically inelastic processes this new technique is included as an integral part either in the SCEM (whose effectiveness has been proved earlier and is additionally supported by new calculations performed during Phase I) or in the aforementioned new theory, SCACEM, which is expected to be applicable even in those cases when potential surfaces in different electronic states significantly differ from each other.

Mathematical arguments presented in support of the new formalism make it especially attractive for the semiclassical description of reactive encounters. In fact, although the latter may be formally treated within SCEM, they may involve large relative deviations of different potential energy surfaces, thereby leading to errors from employing a simple average Ehrenfest potential. The improved theory, SCACEM, generated in Phase I as a feasible strategy to accurately treat processes involving both electronic inelasticity and

reaction, overcomes this difficulty by running trajectories separately on each potential surface.

Another complication associated with treatment of reactive encounters by means of a single effective potential comes from the fact that stretching motions of interatomic bonds undergo a sharp change when bonds break; in order to select coordinates of quasi-periodic motions one has to refer the vibrations to the appropriate reaction path. Since the reaction path varies from one potential surface to another, it requires use of different variables for different potential surfaces; this is relatively easy to implement in the frame of the new theory. The new theory also enables to describe tunneling effects along the streamline coordinate, including a certain type of resonances.

During Phase I the applicability of the developed semiclassical theory has been tested and validated for a two-dimensional representation of vibrationa! excitation in O+HF and Na+H$_2$ collisions for which we can generate exact quantum results. These successful applications encourage further exploration of the technique in realistic multidimensional applications.
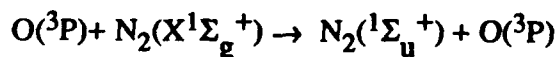
In conclusion, Phase I research has (1) revealed that reliable *ab initio* quantum chemical input can be obtained for SPURC-related systems, (2) established that elementary computational modules required to build the necessary dynamical treatments for SPURC-related rate computations are reliable (Appendix 2), (3) resulted in a significant theoretical break-trough in development of the methodology capable to provide the nuclear state-to-state information that both SPURC and CHARM ultimately need. It is also clear that further systematic method refinement is essential since this type of computational input is valuable to the USAF due to the cost and difficulties for experimental determination of the required data. Towards this end an extended semiclassical theoretical methodology based on the eikonal wavefunction ansatz (Appendix 1) should be employed.

Phase I Results

1.   SPURC-related system survey

The three candidate molecules considered were OH, NO, and N$_2$. Correlation diagrams for the following processes leading to the production of excited species were examined:

$$O(^3P) + N_2 \rightarrow NO(^2\Sigma^+) + N(^4S)$$

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$$O(^3P) + H_2 \rightarrow OH(^2\Sigma^+) + H(^2S)$$

$$O(^3P) + N_2(X^1\Sigma_g^+) \rightarrow N_2(^1\Sigma_u^+) + O(^3P)$$

Details of the pertinent electronic states, dominant interelectronic state couplings, and the likely dynamical pathways for the production of the excited species were analyzed. The feasibility of obtaining the quantum chemical input was examined, and the conclusion is that accurate surfaces can be obtained for the (O,H_2) system, with useable although less accurate surfaces for other systems. We also point out that some of the processes emerging from the recent kinetics work[8] at Aerospace Corporation reveal important electronic energy transfer processes relevant to UV signatures, and we believe that a theoretical treatment can provide useful information to augment the experimental data. Figure 1 is a schematic of the correlation of fragment molecule states important for the (O,H_2) system. Figure 2 provides similar information for the (O,N_2) system.

2. Eikonal Wavefunction Method

Theory Development

The formal issues to be examined in Phase I were:

(i) development of prescriptions for continuation of global semiclassical wavefunctions through classical turning points,

(ii) development of a practical numerical algorithm to extract final populations of vibrational levels from the semiclassical outgoing solution,

(iii) implementation of the single-surface developments (i), (ii) in the multichannel theory with valid use of the Ehrenfest effective potential (SCEM),

(iiii) exploration of means to go beyond the assumptions underlying SCEM to take into account specific topology of the adiabatic potential surfaces, especially responsible for tunneling and related resonances which gave rise to the new multichannel semiclassical theory referred to as SCACEM.

The details of Phase I formal developments on all these issues are covered in the formalism

paper included as Appendix 1. Here we briefly summarize the highlights of these developments in less mathematical terms.
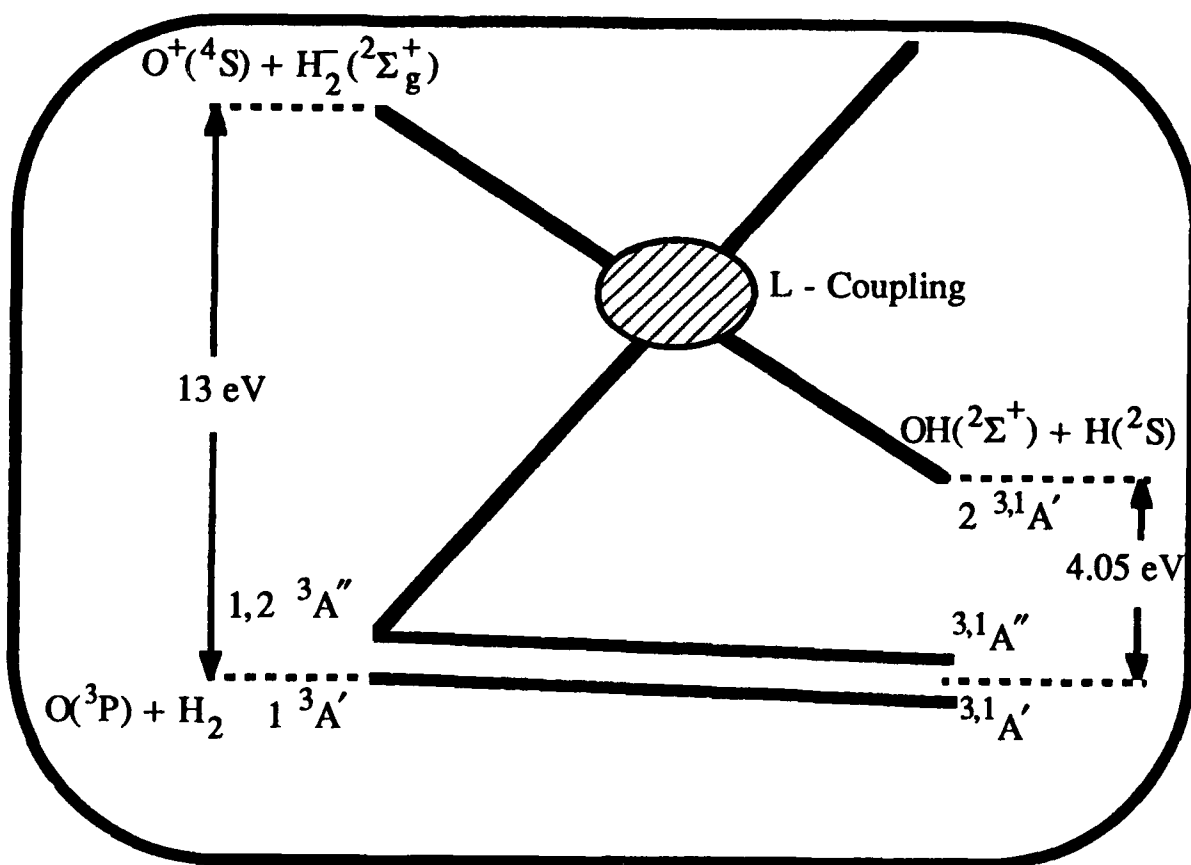

Figure 1. Electronic correlation diagram (C_s symmetry) for low-lying states of the $O(^3P) + H_2$ system.

Adiabatic Approximation of Nuclear Motions in the Semiclassical Picture

When the primary reason for failure of classical mechanics is due to interference effects between amplitudes along different trajectories (this is typically the case when tunneling and curve crossing are unimportant), semiclassical techniques have shown the potential to provide a very efficient computational route that is more accurate than classical mechanics and less expensive than quantal methods. Their main advantage is that propagation of wavefunctions along classical trajectories is governed by a set of ordinary differential equations of the first order which is much easier to solve, compared with the Schroedinger equation. There is however a serious obstacle that damped any progress in
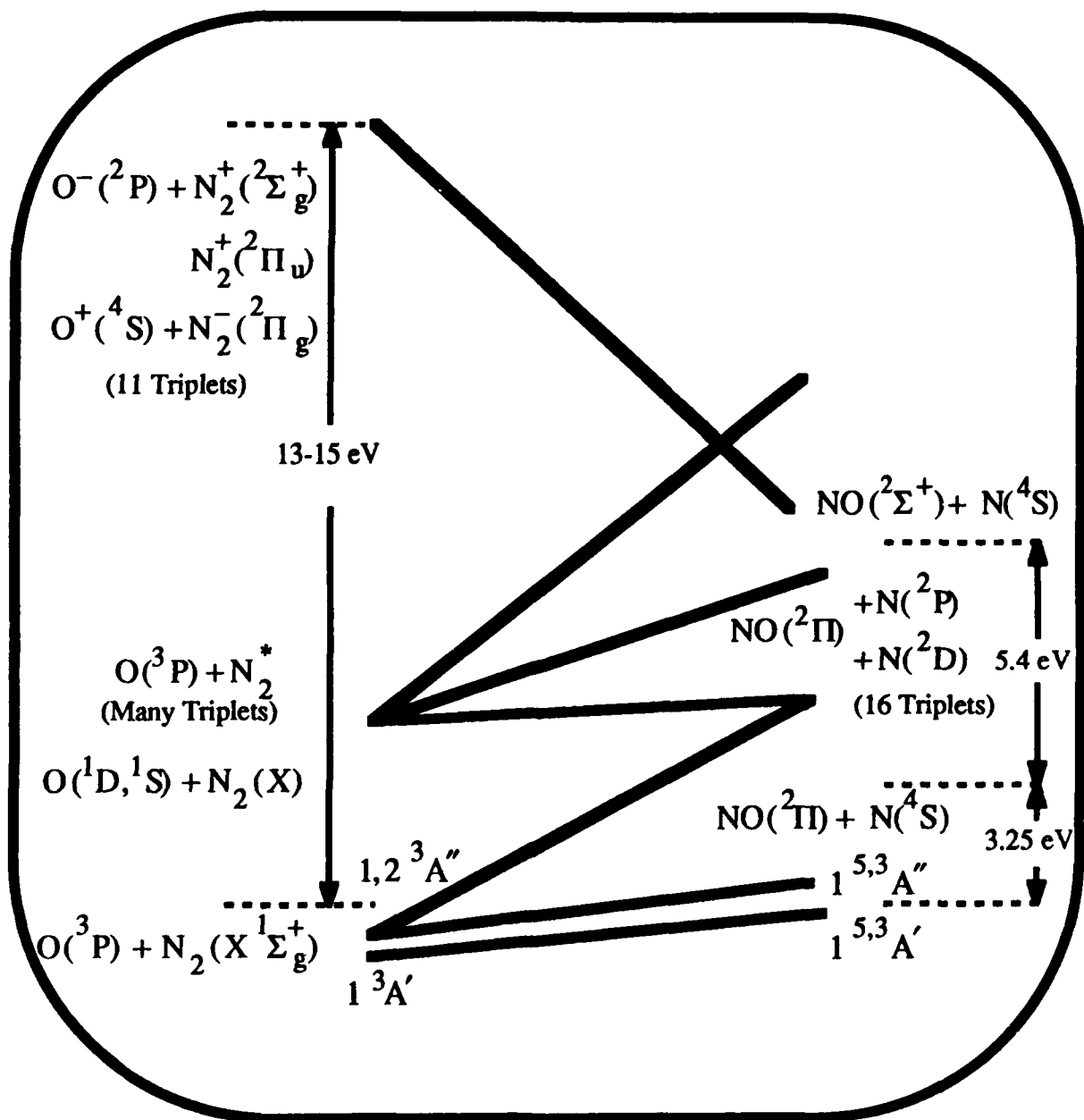
O$^-$(^{2}P) + N$_2^+$($^2\Sigma_g^+$)

N$_2^+$($^2\Pi_u$)

O$^+$(^{4}S) + N$_2^-$($^2\Pi_g$)

(11 Triplets)

13-15 eV

NO($^2\Sigma^+$)+ N(^{4}S)

NO($^2\Pi$) $+$N(^{2}P)

$+$N(^{2}D)   5.4 eV

(16 Triplets)

O(^{3}P) + N$_2^*$
(Many Triplets)

O(^{1}D,^{1}S) + N$_2$(X)

NO($^2\Pi$) + N(^{4}S)   3.25 eV

1,2 ^{3}A''

1 ^{5,3}A''

1 ^{5,3}A'

O(^{3}P) + N$_2$(X $^1\Sigma_g^+$)

1 ^{3}A'

Figure 2. Electronic correlation diagram (C$_s$ symmetry) for states of the {O(^{3}P), N$_2$}system.

     this direction for many years -- the semiclassical approximation breaks down for low velocities such as those experienced when the system hits a potential wall or barrier. In one-dimensional systems the problem is easily corrected using standard WKB connection formulae to carry the solutions through those turning points into classically forbidden regions. Multidimensional systems present a much more difficult problem because the probability density may flow from one degree of freedom to another and hence

one can no longer take advantage of flux conservation to connect incoming and outgoing solutions.

At the present there are no practical numerical algorithms for the general solution of this problem. To by-pass the difficulties coming from the turning points we restrict our analysis to adiabatically separable motions so that one can apply the WKB-connection formulae for each degree of freedom, namely, we subtract $\pi/2$ from the Hamilton characteristic function each time when one of the conjugate momenta changes its sign.

As discussed in Appendix 1 there are two practical problems which can be immediately treated in such a way: nonreactive atom-diatom scattering and scattering of diatomic molecules by a surface. To illustrate the specifics of adiabatic separation of nuclear motions in the semiclassical theory, let us consider atom-diatom collisions with zero angular momentum. Relative oscillations of two atoms and the nutation of the diatom give us two quasi-periodic degrees of freedom. As stretching vibration, described by the variable r, usually has a much larger frequency than the nutation, we treat the former as a quasi-periodic motion with a frequency parametrically dependent on the nutational angle θ and the streamline coordinate R. On the other hand, the nutation is expected to be faster than streamline motion so that we can describe it as quasi-periodic motion with the frequency dependent parametrically on R. We thus neglect the effect of small-amplitude oscillations of the interatomic distance r on the nutation of the diatomic and treat the diatomic as a rigid linear rotator in this particular context. It is important that one needs these assumptions only to formulate the connection formulas for the asymptotic solutions and we do not make any approximations in the classical hamiltonian itself to be consistent with these assumptions.

An extension of the developed technique to describe reactive scattering of two polyatomic fragments is a more sophisticated problem which will be treated within the reaction-path formalism.

Numerical Evaluation of the S-Matrix Elements

Singularity of semiclassical wavefunctions in turning points gives rise to another problem -- a very slow convergence of the their overlaps with quantum mechanical vibrational wavefunctions used to evaluate final populations of vibrational levels. To overcome the numerical difficulties associated with it we developed a new mathematical scheme by formally transforming the (N-1)-dimensional integral, used for evaluation of the

S-matrix element for a scattering process with N-1 quasi-periodic degrees of freedom, into a N-dimensional integral such that singularities of the semiclassical wavefunction is compensated by zeros of the Jacobian in the N-dimensional volume element. The appropriate mathematical details are given in Section VI in Appendix 1.

Self-Consistent Eikonal Method (SCEM) in Applications to Multidimensional Problems

Finally, for electronically inelastic systems, we recommend that the specified multidimensional nuclear wavefunction be combined with the self-consistently calculated electronic amplitudes to obtain the overall (electronic+nuclear) state-to-state transition amplitudes including interference effects. Section IV in Appendix 1 outlines the main features of the SCEM propagating trajectories in the field of a single average potential. It was shown that SCEM corresponds to a very natural physical picture, namely, the flows of the probability density on different adiabatic potential surfaces are approximated by the average flow obtained by weighting the individual flows with the probabilities for the system to be in the appropriate electronic state. We also revealed some additional terms in the potential forces governing nuclear motions in the case of a system with two or more degrees of freedom and suggested the numerical algorithm for their evaluation (see Appendix A in the enclosed formalism paper referred to above as "Appendix 1"). Significance of those terms for SPURC-related applications is expected to be studied in more details in future research.

SCEM may be employed for the nonreactive curve-crossing parts to propagate the wavefunction amplitudes up to a reactive region where the single-surface methods such as variational transition state theory (VTST) can continue the computations to yield the required rate constants. An advantage of using VTST is that one avoids the necessary developments to treat the tunneling in directions perpendicular to the reaction path. Remember that VTST has developed the reliable recipes to treat this effect with a sufficient accuracy whereas including it in the semiclassical technique is a relatively complicated problem. Ideally, for SPURC problems, it will be necessary to propagate SCEM amplitudes through the nonadiabatic region and to use the constructed semiclassical wavefunctions to extract initial populations of states for the single-channel problem in the reactive region.

Self-Consistent Adiabatically-Corrected Eikonal Method (SCACEM)

The necessary state-to state information can be obtained from the new extended theory, SCACEM, which exploits the eikonal ansatz for nuclear wavefunctions in each electronic state, where each wavefunction is propagated now along its own trajectory run on the appropriate adiabatic potential surface. The new formalism is the most significant development arising from Phase I for SPURC and was developed to address situations where the Ehrenfest effective potential used in SCEM can lead to inaccuracies. For example, it may be anticipated that the Ehrenfest effective potential employed in SCEM can be inaccurate when a reactive barrier region appears only on one of the electronic surfaces.

One of the advantages of propagating classical trajectories on the particular adiabatic surfaces as prescribed by SCACEM is that additional approximations are made only in the nonadiabatic region. The equations beyond this region are the exact limit of the Schroedinger equation in the adiabatic representation as $\hbar$ tends to zero and hence their solutions reproduce asymptotically specific features of the exact wavefunctions caused by local topology of the adiabatic potential surfaces. In particular, the new technique makes it possible to trei t tunneling along the streamline coordinate R in electronically inelastic processes provided it takes place beyond the region of strong nonadiabatic couplings.

Let us consider as an example three lowest adiabatic surfaces for $Na+H_2$ C_{2v} encounters. Fig.3 represents the potential surfaces reported by Eakes[9] for the H-H distance equal to $1.4a_0$. We consider collisions with energies 2.2-2.5eV between the bottom and the barrier on the upper curve. We start propagation at a large value of R where two excited electronic states strongly interact with each other so that the probability density flows from the initially populated excited state to the second one. In the region where the trajectory run on the upper surface hits the potential barrier the nonadiabatic interactions become negligible and we can evaluate the reflection coefficient by using the standard formulae of the one-dimensional tunneling theory[10]. As for the trajectory on the lower excited electronic surface it comes back after hitting the potential wall at $R=3a_0$ and then both flows start interfering again with each other. Obviously if the upper potential well has quasi-bound states they manifest as resonances in the scattering amplitudes evaluated according to the outlined recipe.
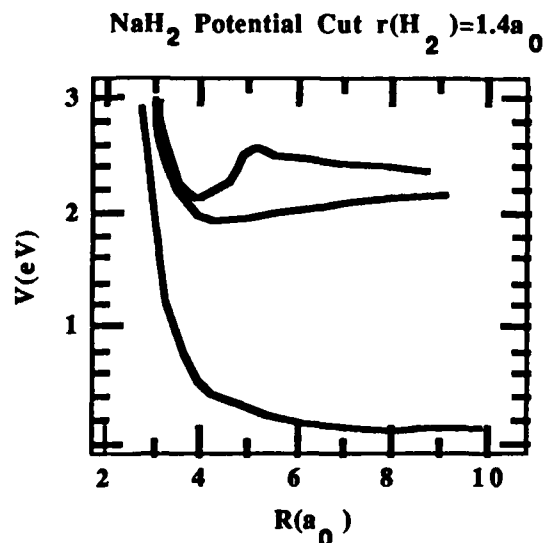
NaH$_2$ Potential Cut r(H$_2$)=1.4a$_0$

Figure 3. Na + H$_2$ potentials for C$_{2v}$ approach of Na.

Computational implementation of SCACEM and tests to reveal its potential for the problems on hand should be considered as one of the most important tasks in the future research.

Numerical Work

The best route to establish the feasibility of approximate semiclassical wavefunction computations is by direct verification in applications to specific benchmark systems for which exact quantum-mechanical results are available. To test the developed algorithms we used the two-dimensional model obtained from the multidimensional Schroedinger equation in the IOS approximation. The exact calculations with such a model for vibrational excitation of HF in collisions with oxygen have been reported earlier by us and moreover any new necessary results could be easily generated by using the available quantum code. For a similar reason we chose to study the Na+H$_2$ as another example. This system is more relevant to the SPURC-related programs as the hydrogen molecules may undergo nonadiabatic transitions. However the latter feature makes exact quantum mechanical calculations much more complicated even in their simplest two-dimensional reduction so that the converged exact solutions could be obtained up to now only for vibrational excitation of H$_2$ in the ground electronic state. We thus had to restrict our analysis at this stage only to those electronically-elastic processes. It is worth emphasizing that, despite the simplicity of the model used for our tests it has inherited the main problem of the

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multidimensional semiclassical theory -- its break-down on the boundary of the classically allowed region.

Compared with the one-dimensional case, the probability density is now redistributed between different trajectories, leading to nonconservation of the flux at the moment the trajectory hits the boundary surface. As an extension of our approach to more realistic systems requires solution of mathematical difficulties similar to those we have addressed in this research, the method does have the potential to provide useful information about the dynamics of real collisional processes. The accuracy of this information for realistic multidimensional applications is now being tested for rotationally inelastic scattering of NO by an uncorrugated silver surface -- the example earlier treated by us using rotonic expansions.

At the very outset, the key feasibility issue to be addressed in Phase I was identified to be the validation of the semiclassical eikonal wavefunction route for computing nuclear state-to-state collisional excitation propensities. Two examples of collisional excitation of vibrational excited states were chosen for which exact quantum limit results were available. These are O+HF and Na+H$_2$ collisions treated within a rotational infinite order sudden (IOS) model. The QIOS (quantal infinite order sudden) models are typically the largest available computations for most systems owing to the proliferation of rotational channels and they do contain the essential physics of vibrational excitation dynamics which is what the eikonal wavefunction was being tested for its ability to describe.

Phase I numerical work focused on two distinct relevant subtasks:

(1) method development for computing S-matrices using semiclassical eikonal wavefunction solutions constructed from nuclear trajectories, thus including quantal interference effects for nuclear motions (numerical tests were based on an implementation for O+HF collisions leading to vibrational excitations), and

(2) numerical tests on a SCEM treatment of atom-diatom collisions which used a vibronic expansion (thus quantum mechanically treating vibrations) while classically treating translation and within the rotational infinite order sudden model of O+HF(v) → O+HF(v') as well as Na+H$_2$(v) → Na+H$_2$(v') collisions. The treatment employed here is often known as the coupled states treatment and is another way of obtaining nuclear state-to-state information along with electronic state-to-state information.

The dynamical model (1) is called the SIOS (for semiclassical infinite-order-sudden) model and (2) is called the RSVE (for rotational sudden with vibronic expansion) model. Appendix 2 has a preliminary draft for a paper resulting from these numerical studies. The key result, represented by the data in Fig. 4, is that even a modest calculation (employing 20 trajectories) within the SIOS model is able to obtain very good prediction of microscopic vibrational excitation probabilities, thereby implying that reliable state-to-state vibrational excitation cross sections will result from such a computation.
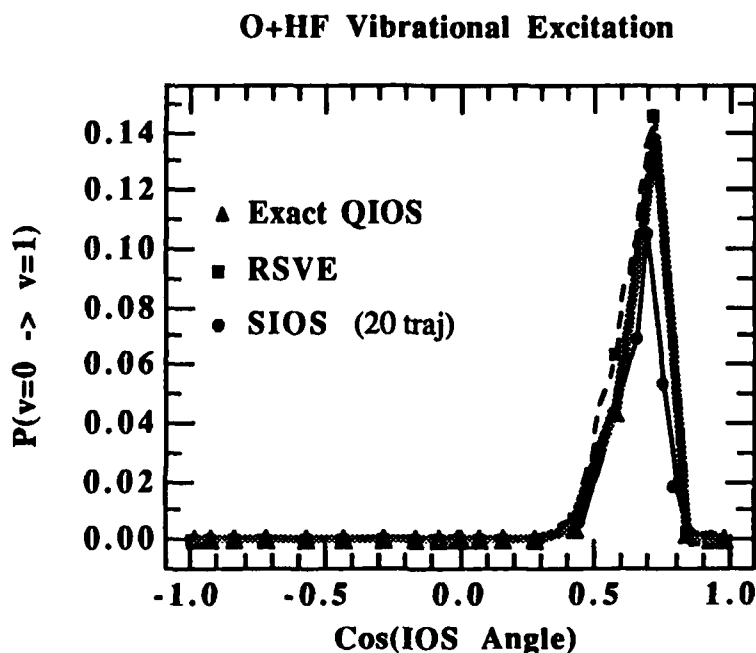
O+HF Vibrational Excitation

Figure 4. Benchmark based on rotational infinite order sudden (IOS) angle-dependent probabilities for v=0 -> v=1 vibrational excitation in $O(^3P)+HF(v=0,j=0)$ collisions at E_{tr}=3.0eV, for total angular momentum, L=0. QIOS denotes exact quantum IOS calculation, RSVE denotes rotational sudden with vibrational expansion, and SIOS denotes semiclassical infinite order sudden. SIOS results are based on semiclassical eikonal wavefunctions (obtained here from a meagre 20 classical trajectories and hence expected to improve) and promise the practically most attractive route for these excitation propensities in signature problems.

The results shown in Fig. 4 are for relatively low values of probabilities (near threshold) and this is a crucial aspect required of a dynamical method to be useful for signature problems: the rationale is that larger Boltzmann weights come in for lower energies and thus the low-intermediate energy contribution has a significant role to play in the observed IR/UV signature. Such velocity components are present to some degree in plume flowfields involving even hypersonic vehicles. The present method offers a

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significant improvement over the previously available classical trajectory method in this regard. The RSVE method is also seen to be successful, but here we stress the new SIOS route which is much more economical and has the potential to scale up to much larger polyatomic problems, a regime where the basis set expansion methods become unwieldy.

List of Publications

The following manuscripts resulted from research supported under the present Phase I contract and are included as appendices to this report.

1. G. A. Natanson and P. K. Swaminathan, "Semiclassical Methodology for Computing Multichannel Eikonal Wavefunctions in Molecular Collisions: A Reformulation and Extension"

2. G. A. Natanson, P. K. Swaminathan, B. C. Garrett and M. J. Redmon, "Accurate Computations of Energy Transfer in Atom-Diatom Collisions: Comparative Study of Vibrational Excitations using Semiclassical Wavefunctions and Coupled Quantal States"

Acknowledgement

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Appendix 1

SEMICLASSICAL METHODOLOGY FOR COMPUTING MULTICHANNEL EIKONAL
WAVEFUNCTIONS IN MOLECULAR COLLISIONS: A REFORMULATION AND
EXTENSION

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I. Introduction

The standard quantum-mechanical description of collisional processes is based on the adiabatic separation of nuclear and electronic motions, assuming that the electrons instantaneously adjust to neaclear motions because of a large difference in their masses. Encounters taking place on a single adiabatic surface can be described in the zeroth approximation simply by the classical equations of motion. However transitions from one electronic surface to another are essentially quantum-mechanical processes which have no analogs in classical mechanics. As numerical solution of the Schroedinger equation is near the capability limit of modern computers even for four-atom collisions on a single potential surface[1] the prospects of obtaining the reliable information for nonadiabatic processes do not seem rather promising at the present.

The gap between the quantum and classical treatments can be however filled by the semiclassical theory. Construction of semiclassical solutions is simpler compared with solving the Schroedinger equation because they are governed by ordinary differential equations of the first order (instead of partial differential equations exploited in quantum mechanics). On the other hand, the semiclassical sheory is accurate enough to reproduce specific quantum-mechanical features which are completely absent in the classical picture. In particular the semiclassical theory turns out to be powerful enough to describe the nonadiabatic transitions which are the main concern in the present research.

There is however an essential obstacle that has been damping a progress in this area for many years. The semiclassical equations imply that higher-order corrections are negligible compared with the kinetic energy the system has so that they break down each time when the latter becomes small as it takes place at classical turning points where semiclassical wavefunctions are singular. The one-dimensional problem has the well-known solution in terms of the so-called WKB method[2] that gives the recipe of how to continue the semiclassical wavefunction after its reflection in the turning point. This recipe however essentially exploits conservation of the flux to connect the incoming and outgoing waves which is insufficient in the multi-dimensional case as there may be exchange of the probability density between different degrees of freedom. The current state-of-the-art theory in this area is mainly developed at the level of formal theorems[3] which prove existence of solutions, but do not provide any practical numerical algorithms to find them. We can cite only a few works[4,5] where the semiclassical scattering theory in many dimensions was brought to the particular applications.

An additional problem arises when one applies the semiclassical technique to nonadiabatic processes. It comes from the interference between wavefunctions propagated on different potential

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surfaces. To take into account this effect one needs to locate on each surface the trajectory that goes through the given point in space which is numerically unaccessable.

Up to now a much more attention has been to given an alternative direction exploiting angle-action variables, in following pioneering works of Marcus[6] and Miller[7] however the reported success in this direction is also very limited. Even disregading the fact that this most popular approach is related with the Schroedinger equation only through the Correspondence Principle and hence it remains unclear to what extent its predictions are equivalent to those of the asymptotic semiclassical theory[3,8] there is a pure practical reason for development of the semiclassical theory in space -- representation of realistic potential surfaces in angle-action variables is a complicated computational problem that makes the whole scheme unfeasible for applications.

The present research makes a significant progress in overcoming two most serious problems of the nonadiabatic semiclassical theory, making possible its practical implementation. The assumption about adiabatic separation of nuclear motions in the semiclassical picture allows us to connect incoming and outgoing semiclassical solutions, reproducing correctly interference effects between different trajectories. Validity of the adiabatic separation of streamline and vibrational motions is demonstrated by comparing the semiclassical and exact quantum-mechanical results for the two-dimensional model describing vibrational energy transfer in an atom-diatom collision in the IOS approximation[9].

Including the adiabatic hypothesis into the Self-Consistent Eikonal Method (SCEM)[10] gave us a practical tool for treating electronically inelastic processes with a few degree of freedom. It was shown that SCEM corresponds to a very natural physical picture, namely, the flows of the probability density on different adiabatic potential surfaces are approximated by the average flow obtained by weighting the individulal flows with the probabilities for the system to be in the appropriate electronic state. We also revealed some additional terms in the potential forces governing nuclear motions in the case of a system with two or more degrees of freedom and suggested the numerical algorithm for their evaluation.

We also developed a new extended approach called SCACEM (Self-Consistent Adiabatically-Corrected Eikonal Method) for a more accurate treatment of electronic inelasticity in molecular collisions; this goes beyond the Ehrenfest effective potential approximation employed in SCEM without compromising on the advantages of the latter method. The new extended theory also exploits the eikonal ansatz for nuclear wavefunctions in each electronic state but each wavefunction is propagated now along its own trajectory run on the appropriate adiabatic potential surface. One of the advantages of propagating classical trajectories on the particular adiabatic surfaces as prescribed by SCACEM is that additional approximations are made only in the nonadiabatic region. The equations beyond this region are the exact limit of the Schroedinger equation in the adiabatic representation as ℏ tends to zero and hence their solutions reproduce

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asymptotically specific features of the exact wavefunctions caused by local topology of the adiabatic potential surfaces. In particular, the developed technique makes it possible to treat tunneling along the streamline coordinate R in ellectronically inelastic processes provided it takes place beyond the region of strong nonadiabatic couplings.

II.Semiclassical multichannel approximation in the mixed adiabatic/diabatic representation

Let us consider the multichannel problem described by a set of linear partial differential equations of the second order:

$$\left[\left(-\frac{\hbar^2}{2}\Delta_Q - E\right)\underline{\underline{1}} + \underline{\underline{V}}(Q) - \hbar^2 \underline{\underline{\vec{F}}}(Q) \bullet \vec{\nabla} + \underline{\underline{H}}(Q)\right] \underline{\psi} = \underline{0} \ , \qquad (2.1)$$

where $\underline{\psi}(Q)$ is the column formed by the functions $\psi_1(Q)$, $\psi_2(Q)$, ...,$\psi_n(Q)$ sought for,

$$\Delta_Q = \sum_{\mu,\mu'} g^{-1/2} \frac{\partial}{\partial Q^\mu} g^{1/2} g^{\mu\mu'} \frac{\partial}{\partial Q^{\mu'}} \qquad (2.2)$$

and $\vec{\nabla}$ are respectively the covariant Laplacian (see next Section for comments) and the gradient in the space of curvilinear coordinates Q (see next Section for comments), $\underline{\underline{V}}(Q)$ is a n x n diagonal matrix having some potentials $V_v(Q)$ as its diagonal elements, $\underline{\underline{H}}(Q)$ is the matrix of potential coupling having zeros at its main diagonal; the components of the vector $\vec{F}$ are n x n real antisymmetric matrices describing nonadiabatic couplings. In the adiabatic representation $V_v(Q)$ are the adiabatic potentials and the matrix $\underline{\underline{H}}(Q) \cong \underline{\underline{0}}$ so that

$$\left[\left(-\frac{\hbar^2}{2}\Delta_Q - E\right)\underline{\underline{1}} + \underline{\underline{V}}(Q) - \hbar^2 \underline{\underline{\vec{F}}}(Q) \bullet \vec{\nabla}\right] \underline{\psi} = \underline{0} \ . \qquad (2.3)$$

The main advantage of the adiabatic representation is that the last term in brackets in (2.3) vanishes in the limit as $\hbar \to 0$. As a result we come to the Hamilton-Jacobi equations governed by the adiabatic potentials. We can thus treat the coupling term as a perturbation . We show below that one needs an assumption of such a kind when continuing the semiclassical wavefunction through turning points of quasiperiodic motions. Another alternative is a system with only potential

couplings which are relatively small compared with the potentials $V_v(Q)$. In the one-dimensional case it is sufficient to require that the couplings are negligible near the turning point of the streamline motion. We come to the problem of this type, when treating quasiperiodic degrees of freedom quantum-mechanically by representing the Schroedinger equation:

$$\left(-\frac{\hbar^2}{2}\Delta_Q + V(Q) - E\right)\psi = 0 \tag{2.4}$$

in the matrix form:

$$\left[\left(-\frac{\hbar^2}{2}\frac{d^2}{dR^2} - E\right)\underline{1} + \underline{V}(R) + \underline{H}(R)\right]\underline{\psi} = \underline{0} , \tag{2.5}$$

where R is the streamline coordinate which is assumed to be orthogonal to all others. As a result Eq.(2.4) takes the form:

$$\left[\left(-\frac{\hbar^2}{2}\frac{d^2}{dR^2} + V_0(R) - E\right)\underline{1} + \underline{H}(R)\right]\underline{\psi} = \underline{0} . \tag{2.6}$$

By analogy applying a similar expansion to an electronically inelastic process described by Schroedinger equation (2.2) we come to the set of ordinary differential equations in the mixed representation:

$$\left[\left(-\frac{\hbar^2}{2}\frac{d^2}{dR^2} - E\right)\psi_{vv} - \hbar^2\sum_{v'\neq v}\sum_{v'}F_{vv;v'v'}(R)\frac{d\psi_{v'v'}}{dR} + \sum_{v',s'}U_{vv;v'v'}(R)\psi_{v'v'}\right] = 0 . \tag{2.7}$$

There are two questions which we need to address here. First of all, we construct asymptotic solutions of (2.1) as $\hbar \to 0$. It is a relatively easy problem which can be formulated in an arbitrary set of variables. It is much more difficult to find the connection formulas between different asymptotic solutions. (As stressed by Schiff[11] the asymptotic solutions are of little use to us unless we know how to connect them together.) This part of the problem can be solved only with some additional assumptions concerning the motions under discussions. Here we restrict our discussion to systems with a single unbounded degree of freedom (a streamline motion) coupled with several quasi-periodic degrees of freedom such that each motion has a different time scale.

There may be also some cyclic motions which do not create any difficulties on their own. All the bound motions are uncoupled at large values of the streamline coordinate R and are assumed to be adiabatically separable in the interaction region so that one can apply the usual WKB quantization rule[2].

Let us illustrate the made assumptions , using scattering of a diatomics by an infinitely massive incorrugated surface as an example. The cyclic motions are represented by the precession of the diatomic around the normal drawn from the center of mass of the diatomic to the surface. Relative oscillations of two atoms and the nutation of the diatom give us two quasi-periodic degrees of freedom . As stretching vibration, described by the variable r, usually has a much larger frequency than the nutation we treat the former as a quasi-periodic motion with a frequency parametrically dependent on the nutational angle θ and the streamline coordinate R. On the other hand, the nutation is expected to be faster than streamline motion so that we can describe it as quasi-periodic motion with the frequency dependent parametrically on R. We thus negelect the effect of small-amplitude oscillations of the interatomic distance r on the nutation of the diatomic and treat the diatomic as a rigid linear rotator in this particular context. We shall see below that one needs these assumtions only to formulate the connection formulas for the asymptotic solutions and we do not make any approximations in the classical hamiltonian itself to be consistent with these assumptions.

Note that we included precession in our analysis only to be able to run trajectories in the Cartesian coordinates. One can directly start from the Schroedinger equation expressed in terms of the curvilinear coordinates R, r, θ, The appropriate kinetic-energy operator

$$\hat{T} = - \frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu_r} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta}$$

(2.8)

is very similar to that for the J=0 atom-diatom nonreactive scattering problem:

$$\hat{T} = - \frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2} \left(\frac{1}{\mu_R} + \frac{1}{\mu_r} \right) \frac{1}{\sin\gamma} \frac{\partial}{\partial\gamma} \sin\gamma \frac{\partial}{\partial\gamma}$$

(2.9)

with r is the interatomic distance in the diatomics, γ is the angle between the diatomics and the vector $\underset{\sim}{R}$ drawn from the incident atom to the center of mass of the diatomics and R=| $\underset{\sim}{R}$ |. (Note that the volume elements dR dr $\sin\theta$ dθ and dR dr $\sin\gamma$ dγ are defined in both cases in exacly the same way.) Therefore vibrational excitation of an diatomics in a J=0 collision with an atom and

scattering of diatomic molecules by incorrugated surfaces can be formally treated in terms of the nearly-indentical formalisms.

To extend the theory of semiclassical transition probabilites to multichannel equation (2.1) we start from Dirac-Marcus' representation[6,12] of the wave functions $\psi_1(Q), \psi_2(Q), ..., \psi_n(Q)$ as

$$\psi_v(Q) = A_v(Q) \exp[iW_v(Q)/\hbar] , \quad v=1,2,...,n, \tag{2.10}$$

where $A_v(Q)$ and $W_v(Q)$ are __real__ functions which vary slowly with their arguments.

Substituting (2.10) into (2.1) with

$$\overrightarrow{P}^{(v)}(Q) \equiv \overrightarrow{\nabla} W_v(Q) , \tag{2.11}$$

$$\left|\overrightarrow{P}^{(v)}(Q)\right|^2 \equiv \sum_{\mu,\mu'} P_\mu^{(v)}(Q) \, g^{\mu\mu'}(Q) \, P_{\mu'}^{(v)}(Q) \tag{2.12}$$

and neglecting the terms of the order of $\hbar^2$, we come to the following set of differential equations of the __first__ order:

$$i\frac{\hbar}{2} \, div \left[\psi_v^2 \, \overrightarrow{P}^{(v)}\right] = \psi_v^2\left[V_v - E - \frac{1}{2}\left|\overrightarrow{P}^{(v)}\right|^2\right] - i\hbar\psi_v \sum_{v'\neq v} \overrightarrow{F}_{vv'} \bullet \overrightarrow{P}^{(v')} \psi_{v'} \tag{2.13}$$

referred to below as the Semiclassical Multichannel Equations (SMEs). Note that div here implies use of the covariant derivatives of a vector $\overrightarrow{I}$ so that

$$div \, \overrightarrow{I} = \sum_{\mu,\mu'} g^{-1/2} \frac{\partial}{\partial Q^\mu} g^{1/2} \, g^{\mu\mu'} I_{\mu'} \quad . \tag{2.14}$$

One can easily verify that

$$\frac{1}{2}\left|\overrightarrow{P}^{(v)}(Q)\right|^2 + V_{eff}^{(v)}(Q) = E \tag{2.15}$$

with

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$$V_v^{eff}(Q) \equiv V_v(Q) + \delta V_v(Q) \tag{2.16}$$

and

$$\delta V_v \equiv \hbar \sum_{v' \neq v} \vec{F}_{vv'} \cdot \vec{P}^{(v')} A_v \sin[(W_{v'} + W_v)/\hbar]/A_{v'} \tag{2.17}$$

and hence the function $W_v(Q)$ is Hamilton's characteristic function[13] for effective potential (2.15).

The SMEs have the trivial solution for the single-channel problem:

$$\frac{1}{2}\left|\vec{P}^{(1)}(Q)\right|^2 + V_1(Q) = E \quad , \tag{2.18a}$$

$$div\left[\vec{P}^{(1)} \rho_1\right] = 0 \tag{2.18b}$$

with

$$\rho_1(Q) \equiv A_1^2(Q) \quad . \tag{2.19}$$

However what is taken for free in that case turns in a rather complicated problem if one has to include interference between the channels. Even the initial incoming values of effective potentials (2.16) cannot be unambiguosly determined because the boundary condition for Hamilton's principal function $W_v(Q)$ is known only for the initially populated channel labeled below by index 1. As a result, quantum-mechanical correction (2.17) to the potential governing classical trajectories turns out to be an ill-defined function in the infinite-separation limit.

One of the ways to bypass this difficulty is to neglect quantum-mechanical correction (2.17), compared with the adiabatic potential $V_v(Q)$, bearing in mind that this correction is proportional to $\hbar$ and hence it disappears in the limit $\hbar \rightarrow 0$. In the one-dimensional case the neglect of this correction leads us to the set of ordinary differential equations that can be solved by means of the finite-difference method provided that the coupling coefficients are negligibly small near the turning points and hence one can make use of the standard WKB connection formuale in each channel. The same assumtion is used by us for the streamline motion in the multi-dimensional case however the necessity to solve the set of partial differential equations makes the problem much more complicated. To overcome those difficulties we develop two approximate methods of its solution: Self-Consistent Eikonal Method[10] (SCEM) and the multichannel theory, Selfconsistent

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Adiabatically-Corrected Eikonal Method (SCACEM), both based on using classical trajectories as curvilinear coordinate axes[8]. In next Section we outline this common part of two methods, by representing the the SMEs in this particular curvilinear coordinate system by means of the standard formulas of differential geometry[14].

III. Trajectory-following coordinate system (TFCS)

Let us now express each of Eqs. (2.13b) in terms of its own set of the curvilinear coordinates $q_{(v)} \equiv \{t_{(v)}, w\}$ with w used for the initial values of w on trajectories governed by the potential $V_v(Q)$ and parametrized by the time $t_{(v)}$ (instead of $Q^0 \equiv R$) different for each channel. Making use of the well-known expression for the covariant derivative (see Eq.(6.87) in Ref.14 with $g^{1/2}$ for J here):

$$ div \left[\psi_v^2 \, \vec{p}^{(v)} \right] = \sum_{s,s'} J_v^{-1} \frac{\partial}{\partial q_{(v)}^s} \left[g_{(v)}^{ss'} J_v \, p_{s'}^{(v)} \psi_v^2 \right] \ , \tag{3.1} $$

where $g_{(v)}^{ss'}$ are the coefficients of momemtum coupling in the new set of coordinates, J_v is the Jacobian of the transformation from $q_{(v)}$ to Q (positive by definition) and

$$ p_s^{(v)} \equiv \frac{\partial W_v}{\partial q_{(v)}^s} \ . \tag{3.2} $$

Taking into account that

$$ \dot{q}_{(v)}^s = \sum_{\mu'} g_{(v)}^{ss'} \, p_{s'}^{(v)} \tag{3.3} $$

with

$$ \dot{q}_{(v)}^0 = 1, \tag{3.4a} $$

$$ \dot{q}_{(v)}^s \equiv \dot{w}^s = 0 \qquad \text{for } s \geq 1 \ . \tag{3.4b} $$

we can represent (2.13) as

$$i\hbar \frac{d\zeta_v}{dt_{(v)}} = \left[V_v - E - \frac{1}{2} \left| \vec{P}^{(v)} \right|^2 \right] \zeta_v \qquad (3.5)$$

$$- i\hbar J_v^{1/2} \sum_{v' \neq v} \vec{F}_{vv'} \cdot \vec{P}^{(v')} \zeta_{v'} / J_{v'}^{1/2}$$

where we put

$$\zeta_v(t_{(v)}, w) \equiv J_v^{1/2}(t_{(v)}, w) \, \psi_v(t_{(v)}, w) / A_1(0, w) , \qquad (3.7)$$

with index 1 used for the initially populated channel. Substituting (2.16), (2.17) and (3.7) in (3.6) we find the following equation for the phase W_v:

$$\frac{dW_v}{dt_{(v)}} = 2 \left[E - V_v^{eff}\left(Q_{(v)}[t_{(v)}, w] \right) \right] \qquad (3.8)$$

and hence

$$W_v(t_{(v)}, w_0) = 2 \int_0^{t_{(v)}} dt' \left\{ E - V_v^{eff}\left(Q_{(v)}[t_{(v)}, w] \right) \right\} \qquad (3.9)$$

or, in a more farmiliar form:

$$W_v(t_{(v)}, w_0) = \int_0^{t_{(v)}} \sum_\mu P_\mu^{(v)} \, dQ_{(v)}^\mu . \qquad (3.10)$$

Note that SMEs (2.13) are independent of the particular choice of the curvilinear coordinates Q as we assumed that the semiclassical approximation can be directly applied to covariant Laplacian (2.2). Use of the Podolsky transformation[15] changing the volume element leads to a quantum-mechanical correction of the order of $\hbar^2$ which is negligible compared with the adiabatic potential if the region, where this correction is singular, is classically forbidden. The well-known Langer correction[16] helps to overcome this difficulty for the Coulomb attractive well. In the problems of our interest the complication comes from the nutational motion because the

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appropriate quantum-mechanical correction is singular in linear configurations, forcing the system to stay away from those.

To evaluate the Jacobian J_v we make use of the numerical algorithm developed by Stodden and Micha[17], extending it to the equations of motion in curvilinear coordinates. To be more precise, we put

$$Q_{(v)}^{\mu s} \equiv \frac{\partial Q_{(v)}^{\mu}}{\partial q_{(v)}^{s}} \ , \tag{3.11a}$$

$$P_{\mu s}^{(v)} \equiv \frac{\partial P_{\mu}^{(v)}}{\partial q_{(v)}^{s}} \tag{3.11b}$$

and integrate the equations:

$$\dot{Q}_{(v)}^{\mu s} = \sum_{\mu'} \left[g^{\mu\mu'} \left[Q_{(v)} \right] P_{\mu' s}^{(v)} + P_{\mu'}^{(v)} \sum_{\mu'} Q_{(v)}^{\mu' s} \frac{\partial g_{(v)}^{\mu\mu'}}{\partial Q_{(v)}^{\mu'}} \right], \tag{3.12a}$$

$$\dot{P}_{\mu s}^{(v)} = \sum_{\mu'} \left[P_{\mu' s}^{(v)} \frac{\partial g_{(v)}^{\mu\mu'}}{\partial Q_{(v)}^{\mu'}} + P_{\mu'}^{(v)} \sum_{\mu'} Q_{(v)}^{\mu' s} \frac{\partial^2 g_{(v)}^{\mu\mu'}}{\partial Q_{(v)}^{\mu'} \partial Q_{(v)}^{\mu'}} \right] - \sum_{\mu'} Q_{(v)}^{\mu' s} \frac{\partial^2 V_v}{\partial Q_{(v)}^{\mu} \partial Q_{(v)}^{\mu'}}$$

$$\tag{3.12b}$$

together with the equations of motion:

$$\dot{P}_{\mu}^{(v)} = \sum_{\mu'} \frac{\partial g_{(v)}^{\mu\mu'}}{\partial Q_{(v)}^{\mu'}} P_{\mu'}^{(v)} - \frac{\partial V_v}{\partial Q_{(v)}^{\mu}} \ . \tag{3.13}$$

IV. Self-Consistant Eikonal Method (SCEM)

Let us now introduce the average flow with the kinetic energy given by the relation

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$$\frac{1}{2}P^2(Q) = \frac{1}{2}\sum_v \rho_v(Q)\left|\vec{P}^{(v)}(Q)\right|^2 /\rho(Q) \tag{4.1}$$

with

$$\rho(Q) \equiv \sum_v \rho_v(Q) . \tag{4.2}$$

Multiplying both sides of Eq.(2.15) by ρ_v , summing over v and taking into account that the vector coefficients $\vec{F}_{vv'}$ in (2.17) change their sign under the interchange of v and v' one can easily verify that the function $P(Q)$ satisfies the equation

$$\frac{1}{2}P^2(Q) + \bar{V}(Q) = E \tag{4.3}$$

with

$$\bar{V}(Q) \equiv \sum_v V_v(Q)\rho_v(Q)/\rho(Q) \tag{4.4}$$

and hence we can define the velocity field of the average flow by means of the relation:

$$\vec{P}(Q) \equiv \vec{\nabla} W , \tag{4.5}$$

where $W(Q)$ is Hamilton's characteristic function for the potential $\bar{V}(Q)$, namely,

$$\frac{1}{2}\left|\vec{\nabla} W\right|^2 + \bar{V}(Q) = E . \tag{4.6}$$

Let us now, in following Micha' work[10], write functions (2.10) in the common eikonal form:

$$\psi_v(Q) = \chi_v(Q) \exp[iW(Q)/\hbar] , \tag{4.7}$$

$$\bar{\psi}_v(Q) = \bar{\chi}_v(Q) \exp[iW(Q)/\hbar], \tag{4.7'}$$

where we use tilda to mark the diabatic wavefunctions by tilda to distinguish them from those in the adiabatic represention. We neglect the difference between the Jacobians in Eq.(3.7), writing SMEs (2.8a), (3.7) as

$$i\hbar\frac{d\beta_v}{dt}_{(v)} = \left[V_v - \bar{V} - \frac{1}{2}\left|\vec{\kappa}^{(v)}\right|^2\right]\beta_v + \sum_{v'\neq v}\vec{F}_{vv'}\cdot\left(\vec{P} + \vec{\kappa}^{(v')}\right)\beta_{v'},$$

(4.8)

where we put

$$\beta_v\left(Q_{(v)}\left[t_{(v)}, w\right]\right) \equiv J_v^{1/2}\chi_v ,$$

(4.9)

$$\vec{\kappa}^{(v)}(Q) \equiv \vec{P}^{(v)}(Q) - \vec{P}(Q) .$$

(4.10)

A similar equation in the diabatic representation takes the form

$$\frac{d\tilde{\beta}_v}{dt}_{(v)} = \left[H_{vv} - \bar{V} - \frac{1}{2}\left|\vec{\kappa}^{(v)}\right|^2\right]\tilde{\beta}_v + \sum_{v'\neq v}H_{vv'}\tilde{\beta}_{v'} ,$$

(4.11')

where $H_{vv'}$ are some diabatic potential couplings and tilda is used to distinguish between two representations.

The main idea of the method is to run trajectories on the single potential surface approximating the potential $\bar{V}(Q)$ by means of the relations:

$$\bar{V}(Q) \approx \sum_v V_v(Q)\left|\beta_v^2(Q)\right|/\bar{p}(Q) ,$$

(4.12)

$$\bar{V}(Q) \approx \sum_{v,v'}H_{vv'}\tilde{\beta}_{v'}(Q)\,\tilde{\beta}_v^*(Q)/\bar{p}(Q) ,$$

(4.12')

with

$$\bar{p}(Q) \equiv \sum_v\left|\beta_v^2(Q)\right| = \sum_v\left|\tilde{\beta}_v^2(Q)\right| .$$

(4.13)

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After neglecting the deviations $\vec{\kappa}^{(v)}$ of the momenta $\vec{P}^{(v)}$ from the average $\vec{P}$ which cannot be evaluated on the trajectories in question we thus come to the following equations for the functions $\beta_v(Q)$ and $\tilde{\beta}_v(Q)$:

$$i\hbar\frac{d\beta_v}{dt} = \left[V_v - \bar{V}\right]\beta_v + \sum_{v' \neq v} \vec{F}_{vv'} \cdot \vec{P}\,\beta_{v'} \quad , \qquad (4.14)$$

$$i\hbar\frac{d\tilde{\beta}_v}{dt} = \left[H_{vv} - \bar{V}\right]\tilde{\beta}_v + \sum_{v' \neq v} H_{vv'}\tilde{\beta}_{v'} \quad . \qquad (4.14')$$

Note that both sets of equations conserve the right side of (4.13) along any trajectory governed by the potential $\bar{V}(Q)$. The equations are solved with the boundary conditions:

$$\beta_v(0,w) = \tilde{\beta}_v(0,w) = \delta_{v1}[\rho^0(w)]^{1/2}\exp\left(-ik_1R_0 + iW^0(w)/\hbar\right). \qquad (4.15)$$

Compared with the discussion presented in Section III, a certain simplification of the formalism comes from the fact that potential (4.4) does not contain the ratio of functions $A_v(Q)$ and $A_{v'}(Q)$ and hence one does not have to deal with the indeterminate forms necessary to evaluate the effective potentials V_v at t=0. It is worth pointing out that the neglect of the deviations of the momenta $\vec{P}^{(v)}$ from the average $\vec{P}$ in Eqs.(4.11), (4.11') is the most serious assumption made so far because it changes the asymptotic behavior of wave functions after the couplings between the channels completely turn off. In next Section we show how one can eliminate this deffect by running a separate trajectory in the field of each adiabatic potential, instead of a single trajectory in the field of the average potential $\bar{V}(Q)$.

The set of equations (4.13') have been recently derived by Stodden and Micha[18] in a more tedious.way by evaluating directly the time derivative of Jacobian (3.2). It should be emphasized that although similar sets of coupled differential equations have been derived in the literature, starting from the time dependent Schroedinger equation in either adiabatic[19] or diabatic[20] representations, the crucial difference comes from turning points where the phases of the functions $\beta_v(Q)$ and $\tilde{\beta}_v(Q)$: take a discontinuous change. The novelty of our approach when extended to the multi-dimensional case comes from the explicit use of the time-scale separation to carry those functions through the caustics. We show below that the equations of motion used by us in the multi-dimensional case also differ from those derived by Meyer and Miller[20].

Potential (4.12') has a very interesting feature, namely, its first derivative with respect to time is given by the simple relation:

$$\dot{\bar{V}} \equiv \sum_{v,v'} \vec{P} \cdot \vec{\nabla} H_{vv'} \beta_v \beta_{v'}^* / \bar{\rho} .$$

(4.16)

To prove it we need just represent (4.12') and (4.13') as

$$\bar{V} \equiv \underline{\beta}^+ \underline{\underline{H}} \underline{\beta} / \bar{\rho}$$

(4.17)

and

$$i\hbar \dot{\underline{\beta}} = (\underline{\underline{H}} - \bar{V} \underline{\underline{1}}) \underline{\beta}$$

(4.18)

and then substitute (4.18) in the derivative of (4.17) with respect to t, taking into account that the matrix $\underline{\underline{H}} - \bar{V} \underline{\underline{1}}$ commutes with $\underline{\underline{H}}$. The direct consequence of the proved result is that in the one-dimensional case the trajectories are governed by the Erenfest potential:

$$\dot{P}^1 = \underline{\beta}^+ \frac{d\underline{\underline{H}}}{dQ^1} \underline{\beta} / \bar{\rho} .$$

(4.19)

(We can always make g^{11} equal to a constant $1/\mu_R$ by the appropriate change of variables so that no additional term appears in the equation for the streamline motion.)

The governing potential force in the multi-dimensional case has a more complicated form:

$$F^\mu = \underline{\beta}^+ \frac{\partial \underline{\underline{H}}}{\partial Q^\mu} \underline{\beta} / \bar{\rho} + \sum_{\mu > 0} \frac{\partial w^\mu}{\partial Q^\mu} \left[\left(\underline{\beta}_{,\mu}^+ \underline{\underline{H}} \underline{\beta} + \underline{\beta}^+ \underline{\underline{H}} \underline{\beta}_{,\mu} - \bar{\rho}_{,\mu} \underline{\beta}^+ \underline{\underline{H}} \underline{\beta} / \bar{\rho} \right) / \bar{\rho} \right] ,$$

(4.20)

where we put

$$\underline{\beta}_{,\mu} \equiv \frac{\partial \underline{\beta}}{\partial w^\mu} , \qquad \bar{\rho}_{,\mu} \equiv \frac{\partial \bar{\rho}}{\partial w^\mu} .$$

(4.21)

Evaluation of derivatives (4.21) along trajectories governed by Erenfest potential (4.12') is discussed in Appendix A.

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V. Selfconsistent Adiabatically-Corrected Eikonal Method (SCACEM)

The most essential obstacle in solving Eqs. (3.6) in the case of more-than-one channels is that the functions $\zeta_{v'}$ with $v' \neq v$ in the right-hand side of (3.6) are supposed to be evaluated on the trajectory $Q_{(v)}[t_{(v)}, w]$. To overcome this difficulty let us first assume that dependence of the nonadiabatic couplings $\vec{F}_{vv'}$ on the quasi-periodic coordinates $Q^1, Q^2,...$ is negligible at large values of the streamline coordinate $R=Q^0$ and only the component $F^0_{vv'}$ along the streamline motion is asymtotically important. As a result of this assumtion SMEs.(2.13) become asymptotically separable. This implies that

$$div \left[\psi_v^2 \, \vec{P}^{(v)} \right]_{R=\infty} = - \hbar k_v(w) \frac{\partial \psi_v^2}{\partial R} \tag{5.1}$$

(where k_1 is just a constant) and hence

$$arg[\psi_v(0, w)] = - ik_v(w)R_0 + iW^0(w)/\hbar + mod(\pi) \quad , \tag{5.2}$$

$$P_\mu^{(v)}(w) = P_\mu^{(1)}(w) \qquad \mu > 0 \, , \tag{5.3}$$

and

$$\hbar k_v(w) = \sqrt{2\mu_R \left[V_1(R_0, w) - V_v(R_0, w) \right] + \hbar^2 k_1^2} \quad . \tag{5.4}$$

We represent now Eqs.(3.6) as

$$i\hbar \dot{R}_{(v_-)}[R,w] \left(\frac{\partial \zeta_v^-}{\partial R} \right)_w = \left[V_v \left(Q_{(v_-)}[R,w] \right) - E - \frac{1}{2} \left| \vec{P}^{(v_-)}[R,w] \right|^2 \right] \zeta_v^-[R,w]$$

$$- i\hbar \sum_{v' \neq v} \frac{J_{v_-}^{1/2}[R,w]}{J_{v_-'}^{1/2}[Q_{(v_-)}]} \vec{F}_{vv'} \left(Q_{(v_-)}[R,w] \right) \bullet \vec{P}^{(v)}[Q_{(v_-)}] e^{i\delta W_v[Q_{(v_-)}]/\hbar} \zeta_v^-[R,w] \quad , \tag{5.5}$$

<div align="center">15</div>

where minus marks the incoming wave, the components $P_\mu^{(v')}[Q_{(v_-)}]$ of the momentum $\vec{P}^{(v')}[Q_{(v_-)}]$, Jacobian $J_{v'}[Q_{(v_-)}]$ and the phase shift $\delta W_v[Q_{(v_-)}]$ are approximated respectively as

$$\sqrt{g^{0\mu}/2}\, P_0^{(v')}[Q_{(v_-)}] = -p_{(v')} - \sqrt{\left[E - V(Q_{(v_-)}) - \frac{1}{2}\sum_{\mu,\mu>0} g^{\mu\mu'} P_\mu^{(v')} P_{\mu'}^{(v')}\right]^2 + p_{(v')}^2}\,,$$

$$(5.6a)$$

$$P_\mu^{(v')}[Q_{(v_-)}] \approx P_\mu^{(v')}[Q_{(v'_-)}]$$

$$(5.6b)$$

$$\pm\left[\sqrt{E - V\left(R, Q^1, \ldots, Q^{\mu-1}, Q_{(v')}^\mu, Q^{\mu+1}, \ldots\right)}\right] - \sqrt{E - V\left(R, Q^1, \ldots, Q^{\mu-1}, Q_{(v)}^\mu, Q^{\mu+1}, \ldots\right)}$$

$$s>0$$

with

$$p_{(v')} \equiv \frac{1}{2}\sum_{\mu>0} g^{0\mu} P_\mu^{(v')}\,,$$

$$(5.7)$$

$$Q^{\mu'}[R, w] \equiv \frac{1}{2}\left(Q_{(v_-)}^{\mu'}[R, w] + Q_{(v'_-)}^{\mu'}[R, w]\right),$$

$$(5.8)$$

$$J_{v'}[Q_{(v_-)}] \approx J_{v'}[Q_{(v'_-)}] \prod_{\mu \geq 0} \frac{P_\mu^{(v')}[Q_{(v_-)}]}{P_\mu^{(v')}[Q_{(v'_-)}]}\,,$$

$$(5.9)$$

$$\delta W_v[Q_{(v_-)}] \equiv \sum_{\mu>0} \int_{Q_{(v')}^\mu}^{Q_{(v)}^\mu} dQ^\mu\, P_\mu^{(v')}[Q_{(v_-)}]\,.$$

$$(5.10)$$

(Sign (+) or (-) in (5.6b) is chosen depending on the direction of the appropriate one-dimensional motion.) We integrate (5.5) by running a set of trajectories on the adiabatic potential surfaces with the initial conditions given by Eqs.(5.3), (5.4) for the momenta and

$$\zeta_v(0, w) = \delta_{v1}[\rho^0(w)]^{1/2} \exp\left(-ik_1 R_0 + iW^0(w)/\hbar\right)$$

(5.11)

for the wavefunctions themselves.

The most important consequence followed from the presented mathematical arguments is that the semiclassical multichannel solution sought for does have the eikonal form -- remember that existence theorems have been proved only for single-channel processes[12] . The equations for the outcoming wave are similar to (5.5) except that they are solved with a diifferent initial conditions formulated using the WKB connection formula at the classical turning point for the streamline motion on the appropriate adiabatic potential surface.

VI. Evaluation of the S-matrix elements from semiclassical wavefunctions

To avoid the singularities at the classical turning points, when evaluating the S-matrix elements:

$$S_{v;v'}^{(v)} = \frac{1}{2}\sqrt{k_{v'}^{(v)}} \, e^{-ik_{v'}^{(v)} R_f} \sum_{\upsilon=\pm1} \int dw \, \psi_{vv}(R_f, w; \upsilon) u_v(w) \, .$$

(6.1)

where $u_v(w)$ is an exact quantum-mechanical wave function and v is a set of the appropriate quantum numbers, we first represent (6.1) as

$$S_{v;v'}^{(v)} \approx \frac{1}{\Delta R} \int_{R_f}^{R_f + \Delta R} dR \, S_{v;v'}^{(v)} \, .$$

(6.2)

The relation turns into the identity if we deal with the exact matrix element which is independent of R. We thus find

$$\Delta R \, \sqrt{k_v^{(v)}} \, S_{v;v'}^{(v)} \approx$$

$$\sum_{\upsilon=\pm1} \int d\tau \sqrt{k^{(\nu)}(w_0,\upsilon)} \int_0^{t_f(w_0,\upsilon)} dt\, \tilde{J}_\nu^{1/2}(t,w_0,\upsilon)\zeta'_{\nu v}(t,w_0,\upsilon)u_{v'}\big(w(t);w_0\big), \tag{6.3}$$

where

$$\zeta'_{\nu v}(t,w_0,\upsilon) \equiv \zeta_{\nu v}(t,w_0,\upsilon)e^{-ik^{(\nu)}(w_0,\upsilon)R(t,w_0,\upsilon)}, \tag{6.4}$$

$$\frac{dw^S}{d\tau^\mu} = P^S(w^S;w_0^S,\upsilon)/m_s \tag{6.5}$$

and $\tilde{J}_\nu$ is the absolute value of determinant of the auxiliary matrix with the elements

$$\tilde{Q}_{(\nu)}^{\mu s} \equiv Q_{(\nu)}^{\mu s}\, P_{(\nu)}^\mu(w_0,\upsilon) \tag{6.6}$$

propagated instead of the functions $Q_{(\nu)}^{\mu s}$ to avoid singularities in the initial conditions for functions (3.11b). (The function $\rho^0(w)$ in (5.11) is chosen in such a way that the matrix element $S_{v;v}^{(1)}$ is equal to 1 for elastic collisions.) The crucial advantage of the integral (6.3) compared with (6.1) is that the Jacobian J_ν appears now in numerator whereas function (6.4) is nonsingular.

Conclusions

The following formal issues were examined:

(i) development of prescriptions for continuation of global semiclassical wavefunctions through classical turning points,

(ii) development of a practical numerical algorithm to extract final populations of vibrational levels from the semiclassical outgoing solution,

(iii) exploration of means to go beyond the assumptions underlying SCEM to take into account specific topology of the adiabatic potential surfaces, especially responsible for tunneling and related resonances which gave rise to the new multichannel semiclassical theory referred to as SCACEM.

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Detailed numerical studies such as the ones[21] in progress are expected to reveal the potential and power of this framework.

Appendix A

The derivatives of w^μ with respect to Q^μ are elements of the matrix $\underset{\approx}{Q}^{-1}$ with $\underset{\approx}{Q}$ formed by the functions

$$Q^{\mu\mu'}_{(\nu)} \equiv \frac{\partial Q^\mu}{\partial q^{\mu'}_{(\nu)}} \, .\tag{A1}$$

We thus come to a <u>nonlinear</u> set of differential equations -- we need to know the derivatives of Q with respect to q to write the equations of motion and we need the equations of motion to evaluate those derivatives. The situation is complitely different from that for the single-channel problem because in the latter case the potential is the known function of coordinates. To decouple the equations we neglect the <u>second</u> derivatives of the functions $\underline{\beta}$, $\bar{p}$ and Q with respect to q. One finds

$$
\dot{P}^{(\nu)}_\mu = \sum_{\mu'} Q^{\mu\mu'}_{(\nu)} \underline{\beta}^{\dagger} \frac{\partial^2 \underline{\underline{H}}}{\partial Q^\mu \partial Q^{\mu'}} \underline{\beta}/\bar{p} + 2\mathrm{Re}\!\left(\underline{\beta}^{\dagger} \frac{\partial \underline{\underline{H}}}{\partial Q^\mu} \underline{\beta}_{,\mu} \right)\!/\bar{p} - \bar{p}_{,\mu} \, \underline{\beta}^{\dagger} \frac{\partial \underline{\underline{H}}}{\partial Q^\mu} \underline{\beta}/\bar{p}^{\,2}
$$

$$
+ 2\sum_{\mu>0} \frac{\partial w^{\mu'}}{\partial Q^\mu}\!\left[\left(\mathrm{Re}(\underline{\beta}^{\dagger}_{,\mu} \, \underline{\underline{H}}\,\underline{\beta}_{,\mu'}) - \bar{p}_{,\mu'}\mathrm{Re}(\underline{\beta}^{\dagger}\,\underline{\underline{H}}\,\underline{\beta}_{,\mu})/\bar{p} \right)\!/\bar{p} + \bar{p}_{,\mu}\bar{p}_{,\nu}\,\underline{\beta}^{\dagger}\,\underline{\underline{H}}\,\underline{\beta}/\bar{p}^{\,3} \right]
$$

$$
+ \sum_{\mu>0} \frac{\partial w^{\mu'}}{\partial Q^\mu}\!\left[\sum_{\mu'} Q^{\mu\mu''}_{(\nu)}\!\left(\underline{\beta}^{\dagger}_{,\mu} \frac{\partial \underline{\underline{H}}}{\partial Q^{\mu''}} \underline{\beta} + \underline{\beta}^{\dagger} \frac{\partial \underline{\underline{H}}}{\partial Q^{\mu''}} \underline{\beta}_{,\mu} - \bar{p}_{,\mu}\underline{\beta}^{\dagger} \frac{\partial \underline{\underline{H}}}{\partial Q^{\mu''}} \underline{\beta}/\bar{p} \right)\!/\bar{p} \right]
\tag{A2}
$$

with

$$P^{\mu\mu'}_{(\nu)} \equiv \frac{\partial P^\mu_{(\nu)}}{\partial q^{\mu'}_{(\nu)}} \, .\tag{A3}$$

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Functions (A1) are then found by integrating the equations:

$$\dot{Q}_{(v)}^{\mu\mu'} = P_{(v)}^{\mu\mu'} \cdot \tag{A4}$$

To take into account the divergence of streamlines we use Eqs.(4.16) only to find the phase of the function $\tilde{\chi}_v(Q)$ whereas its absolute value $\left|\tilde{\beta}_v(Q)\right|$ is evaluated by solving the equations:

$$\frac{d}{dt}(J\,\tilde{\rho}_v) = J \sum_{\mu' \neq \mu} H_{\mu\mu'}\, \mathrm{Im}\left(\chi_{v'}\,\chi_v^*\right) \tag{A5}$$

with

$$\tilde{\chi}_v = \tilde{\rho}_v^{1/2}\,\tilde{\beta}_v / |\tilde{\beta}_v| \tag{A6}$$

and J used for determinant of the matrix $\underset{\approx}{Q}$:

$$J \equiv \frac{\partial(Q)}{\partial(q)} \cdot \tag{A7}$$

A similar scheme can be developed in the adiabatic representation.

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Appendix 2

ACCURATE COMPUTATIONS OF ENERGY TRANSFER IN ATOM-DIATOM
COLLISIONS: COMPARATIVE STUDY OF VIBRATIONAL EXCITATIONS USING
SEMICLASSICAL WAVEFUNCTIONS AND COUPLED QUANTAL STATES

(PRELIMINARY DRAFT for Journal of Chemical Physics)

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I. INTRODUCTION

Molecular collisional energy transfer presents a computationally challenging problem to the dynamicist even after the global potential energy surface is known. A rich variety of quantum mechanical, semiclassical and classical models may be constructed to solve the problem depending on the behavior of the potential energy surface which controls the collision dynamics. The information from modern laser-based experiments, involving precise microscopically detailed observations of collisions, is in the form of state-resolved cross sections and demand an explanation from theory at that level of detail. Classical mechanics in itself does not offer a long-term solution for obtaining such state-resolved information. Fully quantum mechanical treatments become unwieldy for realistic systems despite recent triumphs that exploit efficient algorithms on supercomputers. Thus there is a present-day need to develop and exploit semiclassical dynamical theories that hold promise. In order to obtain general results, it has to be based on a systematic process involving detailed benchmarks against accurate quantum mechanical results for smaller systems and the development of controlled computational schemes which are careful paths to accomplish the devious transcription from classical trajectories to semiclassical wavefunctions.

The present paper reports a study of vibrational excitation during atom-diatom collisions in gas phase and is one of many successful numerical experiments in which we have employed the eikonal ansatz for the semiclassical wavefunction. The relevant general formal discussions have been presented elsewhere in greater detail. The present article will focus on the formulation for the vibrational excitation problem and its numerical investigation.

In this paper we consider a two degree of freedom model of atom-diatom collisions (O+HF and Na+H_2 collisions are studied) as defined in the rotational infinite order sudden (IOS) approximation. The numerical tests presented here are benchmarked against previously existing quantum IOS (QIOS) results. Two distinct dynamical models are employed in this paper to describe state-to-state vibrational dynamics: (1) is based on combining a classical treatment of translational motion with a quantal states expansion in target vibrational states (called RSVE: for rotational sudden with vibronic expansion) and (2) is based on employing semiclassical eikonal wavefunctions for all degrees of freedom

obtained from their classical trajectories (called SIOS: for semiclassical infinite order sudden).

II. THEORY

1.IOS Approximation in the diabatic representation

The rotational IOS approximation[1] for the atom-diatom scattering problem is based on solving the two-dimensional Schroedinger equation with the Hamiltonian:

$$\hat{h}_{IOS} \equiv \left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_{BC}}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2 l(l+1)}{2\mu R^2} + \frac{\hbar^2 j(j+1)}{2\mu_{BC}r^2} \right)\underline{\underline{1}} + \underline{\underline{H}}(R,r,\gamma)$$

$$(1.1)$$

where $\underline{\underline{H}}(R,r,\gamma)$ is the n x n matrix of the diabatic potentials and couplings between different electronic states, R is the distance between the center of mass of the diatomic BC and the atom A, r is the bond length in the diatomic BC and γ is the angle between the diatomic and the radius drown from its center of mass to the atom A.

2. Quantum-mechanical treatment of vibrations.

In following Redmon et. al. [2] we reduce the problem to the infinite set of the ordinary differential equations of the second order by using the matrix representation for the hamiltonian in the space of the vibrational coordinate r, namely, we use the eigenfunctions of the Schroedinger equation:

$$\left[-\frac{\hbar^2}{2\mu_{BC}}\frac{d^2}{dr^2} + V_{BC}(r) + \frac{\hbar^2 j(j+1)}{2\mu_{BC}r^2} - \varepsilon_v^j \right] u_v^j = 0$$

$$(2.1)$$

as the basis set and represent (2.1) as

$$-\frac{d^2\psi_{nv}^{jl}}{dR^2} - k_{jv}^2 \psi_{nv}^{jl} + \sum_{n',v'} h_{nv,n'v}^{jl}(R,\gamma)\psi_{nv'}^{jl} = 0 ,$$

$$(2.2)$$

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where we put

$$h^{jl}_{nv,n'v'}(R,\gamma) \equiv \delta_{nn'}\delta_{vv'}\frac{l(l+1)}{R^2}$$

$$+ \frac{2\mu}{\hbar^2}\left\{ -\Delta D_\eta + \int dr\, u^j_v(r)\, u^j_{v'}(r)\left[H_{nn'}(R,r,\gamma) - \delta_{nn'}V_{BC}(r)\right]\right\} ,$$

(2.3)

with

$$\hbar k_{jv} \equiv \left[2\mu(E - \varepsilon^j_v)\right]^{1/2}$$

(2.4)

and

$$\Delta D_\eta \equiv \lim_{R\to\infty}\left[H_{\eta\eta}(R,r,\gamma) - H_{11}(R,r,\gamma)\right]$$

(2.5)

used to evaluate the probabilities of transitions from the ηth electronic state.

We solve the set of coupled differential equations (2.2) by representing wavefunctions ψ^{jl}_{nv} in the common eikonal form[3]:

$$\psi^{jl}_{nv}(R;\gamma) = \frac{1}{\sqrt{P^{jl}(R;\gamma)}}\beta^{jl}_{nv}(R;\gamma)\, \exp\left[iW^{jl}(R;\gamma)/\hbar\right]$$

(2.6)

where $W^{jl}(R;\gamma)$ is Hamilton's characteristic function[4] found from the Hamilton-Jacobi equation[4]:

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$$\frac{1}{2\mu}\left|P^{jl}(R;\gamma)\right|^2 + \bar{V}^{jl}(R;\gamma) = \frac{1}{2}k^2_{jv} \tag{2.7}$$

with

$$P^{jl} = \frac{dW^{jl}}{dR} \tag{2.8}$$

and $\bar{V}^{jl}(R;\gamma)$ denotes the Ehrenfest potential:

$$\bar{V}^{jl}(R;\gamma) = \sum_{nv,n'v'} h^{jl}_{nv,n'v'}\beta^{jl}_{n'v'}\beta^{jl\,*}_{nv} \Big/ \sum_{nv}\left|\beta^{jl}_{nv}\right|^2 \tag{2.9}$$

The functions β^{jl}_{nv} satisfy the set of coupled equations:

$$i\hbar\beta^{jl}_{nv} = \sum_{nv,n'v'} h^{jl}_{nv,n'v'}\beta^{jl}_{n'v'} - \bar{V}^{jl}\beta^{jl}_{nv} \tag{2.10}$$

and are solved together with the equation of motion for the potential (2.9).

3. Semiclassical treatment of vibrations

A. Equations of Motions

We represent the wavefunction $\psi(R,r;\gamma;lj)$ in the eikonal form:

$$\psi(R,r;\gamma;lj) = A(R,r;\gamma;lj) \exp[iW(R,r;\gamma;lj)/\hbar] \quad , \tag{3.1}$$

where $W(R,r;\gamma;lj)$ is Hamilton's characteristic function:

$$\frac{1}{2\mu}\left(\frac{dW}{dR}\right)^2 + \frac{1}{2\mu_r}\left(\frac{dW}{dr}\right)^2 + U(R,r;\gamma;lj) = E \tag{3.2}$$

for the potential

$$U(R,r;\gamma;lj) \equiv V(R,r;\gamma) + \frac{\hbar^2 l(l+1)}{2\mu R^2} + \frac{\hbar^2 j(j+1)}{2\mu_{BC}r^2} \tag{3.3}$$

The momenta conjugate to the coordinates R and r are given by the relation:

$$P_0(R,r;\gamma;lj) = \frac{dW}{dR}, \quad P_1(R,r;\gamma;lj) = \frac{dW}{dr} \tag{3.4}$$

To carry the wavefunction $\psi(R,r;\gamma;lj)$ through turning points we represent it as

$$\psi(t,r_0;\gamma;lj) \equiv J^{-1/2}(t,r_0;\gamma;lj) \; A(0,r_0;j) \; \zeta(t,r_0;\gamma;lj) \tag{3.5}$$

where t is time, r_0 is the initial value of r on the trajectory run on the potential surface U and $J(t,r_0;\gamma;lj)$ is the Jacobian of the transformation:

$$t,r_0 \rightarrow R(t,r_0;\gamma;lj), \; r(t,r_0;\gamma;lj) \; , \tag{3.6}$$

and then assume[5] that the function $\zeta(t,r_0;\gamma;lj)$ is continuous everywhere by analogy with the one-dimensional case. We, in following Ref.5, solve the equation:

$$i\hbar\frac{d\zeta}{dt} = \left[U - E - \frac{(P_0)^2}{2\mu} - \frac{(P_1)^2}{2\mu_{BC}}\right]\zeta \tag{3.7}$$

as if the function $\zeta(t, r_0; \gamma; lj)$ itself were continious, finally shifting its phase by $\pi/4$ times the total number of the turning points passed.

B. Initial conditons

Let us put $Q^0 \equiv R$, $Q^1 \equiv r$, $w^1 \equiv r_0$,

$$V_j(r) \equiv V_{BC}(r) + \frac{\hbar^2 j(j+1)}{2\mu_{BC}r^2} . \tag{3.8}$$

Then the initial conditions take the form

$$Q^0(0, r_0, \pm 1) \equiv R_0 , \quad Q^1(t_0, r_0, \pm 1) = r_0 . \tag{3.9}$$

$$P^0(t_0, r_0, \pm 1) = -P_{vj} , \quad P^1(t_0, r_0, \pm 1) = \pm p_r(r_0) \tag{3.10}$$

with

$$p_{vj} = \hbar k_{vj} = \sqrt{2\mu(E - \varepsilon_{vj})} \tag{3.11}$$

and

$$p_r(r) \equiv \sqrt{2\mu_{BC}\left[\varepsilon_{vj} - V_j(r)\right]} , \tag{3.12}$$

$$Q_1^0(0, r_0, \pm 1) \equiv 0 , \quad Q_1^1(0, r_0, \pm 1) \equiv 1 \quad , \tag{3.13}$$

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$$P_1^0(t_0, r_0, \pm 1) \equiv 0, \quad P_1^1(0, r_0, \pm 1) = - \frac{\mu_{BC}}{P^1(0, r_0, \pm 1)} \frac{dV_j}{dr}\bigg|_{r=r_0}, \tag{3.14}$$

$$W_0(r_0, \pm 1) = \pm \left[\int_{r_-}^{r_0} dr' p_r(r') - \frac{\pi}{4} \right], \tag{3.15}$$

$$J(0, r_0, \pm 1) \equiv - p_{vj} / \mu, \tag{3.16}$$

$$\psi(0, r_0, \pm 1) = \frac{1}{2} \left[k_{vj} | p_r(r_0) | \right]^{-1/2} e^{iW_0(r_0, \pm 1) - ik_{vj}R_0}, \tag{3.17}$$

$$\zeta(0, r_0, \pm 1) = \frac{1}{2} |J(0, r_0, \pm 1)|^{1/2} e^{iW_0(r_0, \pm 1) - ik_{vj}R_0}. \tag{3.18}$$

c. Connection formulae

If the interaction between vibrational and collisional motions is negligible the derivative of r with respect of its initial value r_0 can be evaluated by differentiating the equation:

$$t = \mu_{BC} \int_{r_0}^{r(t, r_0)} dr'/p_r(r') \tag{3.19}$$

with respect to r_0 at the fixed moment t. We find

$$p_r^{-1}(r) \left(\frac{\partial r}{\partial r_0} \right)_t - p_r^{-1}(r_0) = 0 \tag{3.20}$$

and hence

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$$Q_1^1 \approx \left(\frac{\partial Q_1}{\partial r_0}\right)_t = p_r(r)/p_r(r_0) .$$
(3.21)

Therefore if the off-diagonal element Q_1^0 can be also neglected the Jacobian J factors as

$$\mu J(t,r_0,\pm 1) \approx P^0(t,r_0,\pm 1)P^1(t,r_0,\pm 1)/P^1(t_0,r_0,\pm 1) ,$$
(3.22)

and its zeros approximately coincide with zeros of the momenta P^0 and P^1. We thus assume that jumps of the Jacobian on the caustics are governed for adiabatically separable motions by the standard WKB rules, namely, that the function $|\zeta(Q)|$ is continuous there, whereas the phase of the function $\zeta(Q)$ decreases by $\pi/2$:

$$W(Q) \to W(Q) - \pi/2$$
(3.23)

if the Jacobian changes its sign, and by π, if both momenta change their sign during the same time step.

D. Average of the final amplitudes over the initial conditions

The exact quantum mechanical wave function has the asymptotics:

$$\psi_{vj}(R_f,r) = \frac{u_{vj}(r)}{k_{vj}^{1/2}}e^{-ik_{vj}R_f} + \sum_{v',j'} S_{vj;vj'}\frac{u_{vj'}(r)}{k_{vj'}^{1/2}}e^{ik_{vj'}R_f} ,$$
(3.24)

where the S-matrix elements $S_{vj;vj'}$, for $vj \neq v'j'$ are given by the relation:

$$S_{vj;v'j'} = \sqrt{k_{v'j'}} \, e^{-ik_{v'j'}R_f} \int_0^\infty dr \, \psi_{vj}(R_f,r) u_{v'j'}(r) . \tag{3.25}$$

By analogy with (3.25) we evaluate the semiclassical S-matrix elements by means of the relation:

$$S_{vj;v'j'} = \frac{1}{2}\sqrt{k_{v'j'}} \, e^{-ik_{v'j'}R_f} \sum_{\upsilon=\pm 1} \int_0^\infty dr \, \psi_{vj}(R_f,r;\upsilon) u_{v'j'}(r) . \tag{3.26}$$

To avoid of the singularities in the turning points we first represent this matrix element as the two-dimensional integral using the relation:

$$S_{vj;v'j'} \approx \frac{1}{\Delta R} \int_{R_f}^{R_f+\Delta R} dR \, S_{vj;vj'} . \tag{3.27}$$

(The relation turns into the identity if we deal with the exact matrix element which is independent of R.) Substituting (3.26) into (3.27) we find

$$\Delta R \left(k_{vj} \mu \mu_{BC} C_{vj} \right)^{1/2} S_{vj;v'j'} \tag{3.28}$$

$$= \sum_{\upsilon=\pm 1} \int_{r_-}^{r_+} dr_0 \left[\frac{k(r_0,\upsilon)}{p_r(r_0,\upsilon)} \right]^{1/2} \int_0^{t_f(r_0,\upsilon)} dt \, J^{1/2}(t,r_0,\upsilon) \zeta'_{vj}(t,r_0,\upsilon) u_{v'j'}(r(t);r_0)$$

$$= \frac{1}{\mu_{BC}^{3/4}} \sum_{\upsilon=\pm 1} \int_0^{T/2} d\tau \, k^{1/2}[\tau,\upsilon] \int_0^{t_f[\tau,\upsilon]} dt \, J^{1/2}[t,\tau,\upsilon] \zeta'_{vj}[t,\tau,\upsilon] u_{v'j'}(r(t);r_0(\tau)) ,$$

where

$$\zeta_{vj}(t,r_0,\upsilon) \equiv \zeta_{vj}(t,r_{0'}\upsilon)e^{-ik(r_{0'}\upsilon)R(t,r_{0'}\upsilon)} \qquad (3.29)$$

$$\mathcal{J}(t,r_{0'}\upsilon) \equiv P^1(t_{0'}r_{0'}\upsilon)J(t,r_{0'}\upsilon) = \begin{vmatrix} P^0 & P^1 \\ \tilde{Q}_1^0 & \tilde{Q}_1^1 \end{vmatrix} \qquad (3.30)$$

with

$$\tilde{Q}_1^0(t,r_0,\upsilon) \equiv P^1(t_{0'}r_{0'}\upsilon)Q_1^0(t,r_{0'}\upsilon), \quad \tilde{Q}_1^1(t,r_0,\upsilon) \equiv P^1(t_{0'}r_{0'}\upsilon)Q_1^1(t,r_0,\upsilon) . \qquad (3.31)$$

and the notations $[\tau,\upsilon]$ and $[t,\tau,\upsilon]$ stand for $(r_0(\tau),\upsilon)$ and $(t,r_0(\tau),\upsilon)$. We directly propagate $\tilde{Q}_1^0$ and $\tilde{Q}_1^1$ along the trajectory to avoid possible complications coming from the singularities in (3.14) which appear if the trajectory starts from the turning point.

III. POTENTIAL ENERGY SURFACES

Two candidates of collisional excitation of vibrational levels, (1) in $O(^3P)+HF(v=0,j=0)$ collisions and (2) in $Na(3s^2S)+H_2(v=0,j=0)$ collisions, both of which have previously existing potential energy surface information, were studied. The potential energy surface for the OHF system is based on an earlier UHF calculation[2] and a sum over pairs plus three-body correcting analytical fit (surface 1 of ref. 2) whereas the NaH$_2$ collisions were studied on a DIM potential energy surface.[6] A LEPS fit to MCSCF results for OHF were also generated in ref.2 to enable the dynamical study of the H abstraction reaction but this needs to be employed only at higher energies than presently reported. We refrain from including the analytical and numerical details regarding the potential surfaces for brevity since they are published elsewhere.

A central feature of the OHF potential surface that is relevant for vibrational excitation dynamics is the expected concentration of most of the vibrational excitation (at

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lower energies) to a narrow range of IOS-angles, close to the approach of O atom from the H-atom end, of the HF molecule; in this direction, the potential surface allows a reactive encounter to occur at higher energies. This will be borne out by the dynamics results below. In the case of NaH_2 collisions, only the electronically adiabatic ground surface (obtained from diagonalizing the 8 diabatic DIM surfaces of ref. 6) is employed in the electronically elastic results to be presented below for comparing QIOS and RSVE results.

IV. CALCULATIONAL DETAILS

The RSVE dynamical calculations using eqs. (2.10) are straightforward once the potential matrix in the vibronic basis is setup to be computed. This is done by diagonalizing the asymptotic vibrational Schroedinger equation in a harmonic basis set or employing one of many standard numerical algorithms[1] to obtain the target states. The atom-diatom potential matrix is readily computed along the trajectory since it is expanded in these target states which have amplitudes that vary with time according to eq. (2.10) thereby leading to a time-dependent potential obeying (2.9). The amplitude initial conditions are chosen to correspond to unit probability in the diatomic v=0 state. The separation R is chosen large and the asymptotic negative relative momentum is defined by the channel potential in the v=0 channel and collision energy. The final amplitudes in other state channels resulting from solving the dynamical equations yield the inelastic transition probabilities. The computation of cross sections involves integration over many trajectories that represent varying IOS-angles and impact parameters for each given initial rovibrational state. All the preliminary computations reported here are for initial v=j=0 for the diatomic and the study examines dependence on collision energy and total angular momentum (semiclassically defined by the impact parameter).

The SIOS calculations start with the generation of a bundle of classical trajectories determined by the collision energy and total angular momentum. Only 20 trajectories are employed in the present results. The main task involves building the semiclassical eikonal wavefunction along these trajectories giving special attention to the semiclassical phase changes at caustics (such as classical turning points). The latter are determined by the semiclassical Born Oppenheimer approximation (see previous section and Appendix 2) applied to the present problem. The post-collision eikonal wavefunction is then projected onto selected final states to directly determine the S-matrix elements for inelastic transitions. The projection process employs interpolation of the asymptotic eikonal wavefunction to result in a finely grided numerical quadrature for S-matrix amplitudes since the inelastic

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trajectories end in a nonuniform grid even when the initial conditions start from a uniform grid. Cross section computations involve integration of these amplitudes over IOS-angles and impact parameters and introduce further quantal interference effects.

V. RESULTS AND DISCUSSION

Figure 1 shows that excellent agreement with an exact limit QIOS benchmark is obtainable from the RSVE computations. This success of RSVE in gas phase is consistent with the similar success that the coupled states ansatz has had in treating rotationally-electronically inelastic gas/surface encounters involving up to 282 channels.[7] The most exciting aspect of figure 1 is however the promise shown there by the SIOS method, which is seen to capture the essential physics of this collision; the results shown are from SIOS calculations that employ semiclassical wavefunctions based on a meager 20 trajectories and are not yet numerically the best they can be.

Figures 2 (a and b) show dependence on total angular momentum for the two examples of vibrational excitation studied here. Fig. 2a contains all the data available at the time of this report. (Detailed calculations are in progress to make a full assessment of the methodologies in different L and E_{tr} regimes.) The NaH_2 computations were done to see if the quality of agreement is maintained for a completely different molecular system and Fig. 2b is encouraging (note that H_2 being a homonuclear diatomic molecule is fully studied by sampling half the IOS-angle space compared to HF).

VI. CONCLUDING REMARKS

We have produced a systematic numerical benchmark for collisional excitation of vibrational levels employing semiclassical methods. Two semiclassical computational routes, (1) using a coupled quantal states ansatz to describe vibrational states quantum mechanically and translational motion classically, within the SCEM framework, and (2) using semiclassical wavefunctions generated from classical trajectory results using a newly developed (semiclassical Born-Oppenheimer approximation) procedure were tested against exact quantum limit results. Both the semiclassical methods were successful in obtaining reliable numbers for state-to-state vibrational excitation probabilities. The use of method (2), termed SIOS herein, is indicated as an exciting prospect: such a technique is to be welcomed as a computational route allowing the transformation of information from classical trajectories to state-to-state transition amplitudes at the semiclassical level. The

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novel feature of the SIOS scheme employed here compared to rigorous S-matrix theory of Miller[8] (which was difficult to apply in practical problems and soon went out of use) is that there are no nonlinear root trajectory searches to be performed here; instead, amplitudes are obtained by projecting the eikonal scattering wavefunction on to specific final states. The promise of such a method was demonstrated earlier in the Franck-Condon region for photodissociation,[9] but the present validation for vibrational excitation processes significantly extends the validity regime, by demonstrating that useful quality persists in outgoing eikonal wavefunctions in the asymptotic region provided valid connection formulae are employed.

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Figure Captions

1. Comparison of angle-dependent probabilities for $v=0 \rightarrow v=1$ vibrational excitation in $O(^3P)+HF(v=0,j=0)$ collisions at $E_{tr}=3.0eV$, for total angular momentum, $L=0$. Points are marked by bullets = SIOS, circles = QIOS, and stars = RSVE results.

2. (a) Comparison of RSVE and QIOS results for variation of IOS-angle dependent $v=0 \rightarrow v=1$ probabilities with total angular momentum L at $E_{tr}=3.0eV$ for $O(^3P)+HF(v=0,j=0)$ collisions.

   (b) Comparison of RSVE and QIOS methods for variation of IOS-angle dependent $v=0 \rightarrow v=1$ probabilities with total angular momentum L at $E_{tot} = 0.075$ au for $Na(3s^2S)+H_2(v=0,j=0)$ collisions.

P|Cos(γ)| vs. Cos(γ)
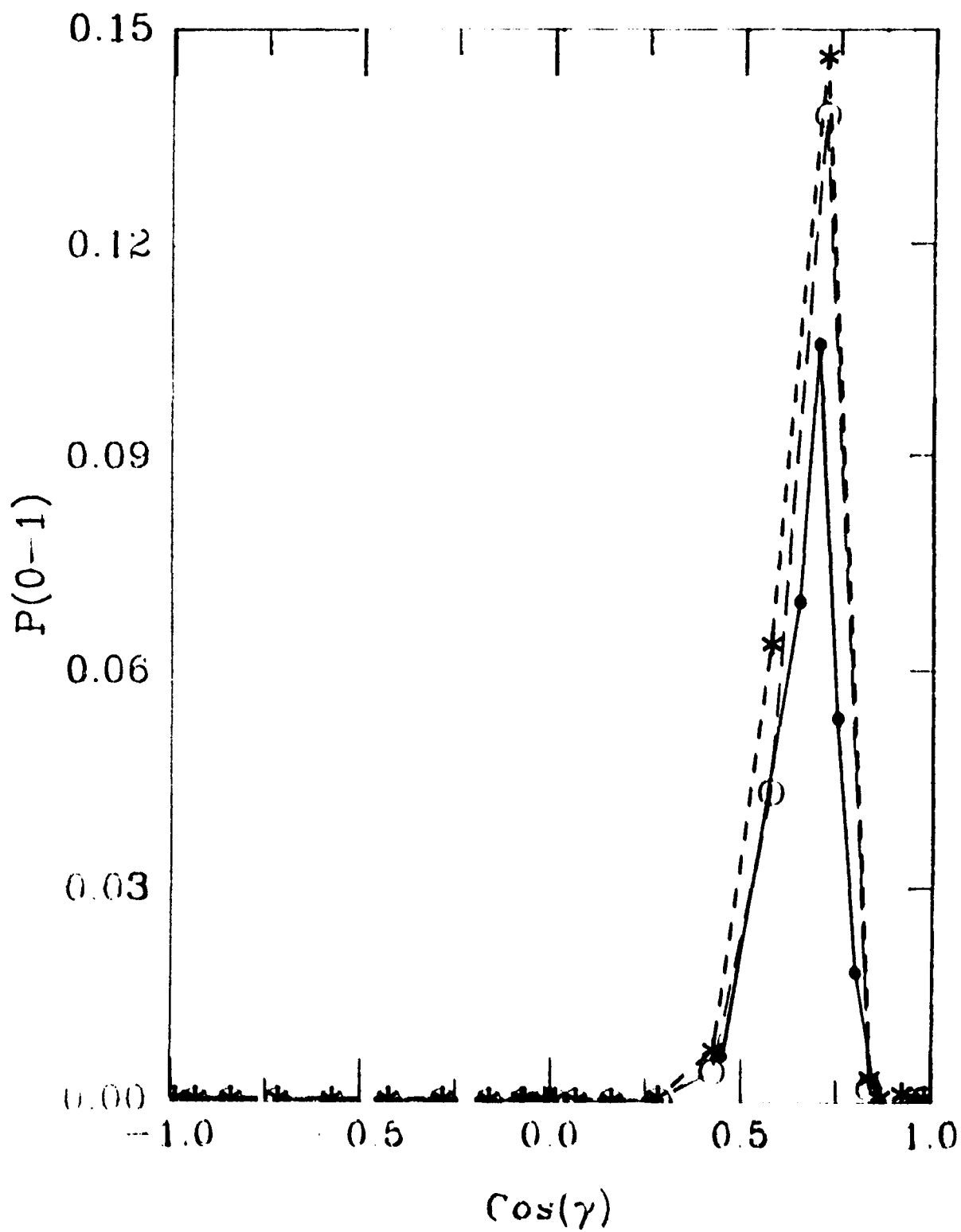
FIGURE 1

P[Cos(γ)] vs. Cos(γ)

FIGURE 2a

QIOS vs. RSVE l-dependent data

P(Cosγ) vs. Cosγ
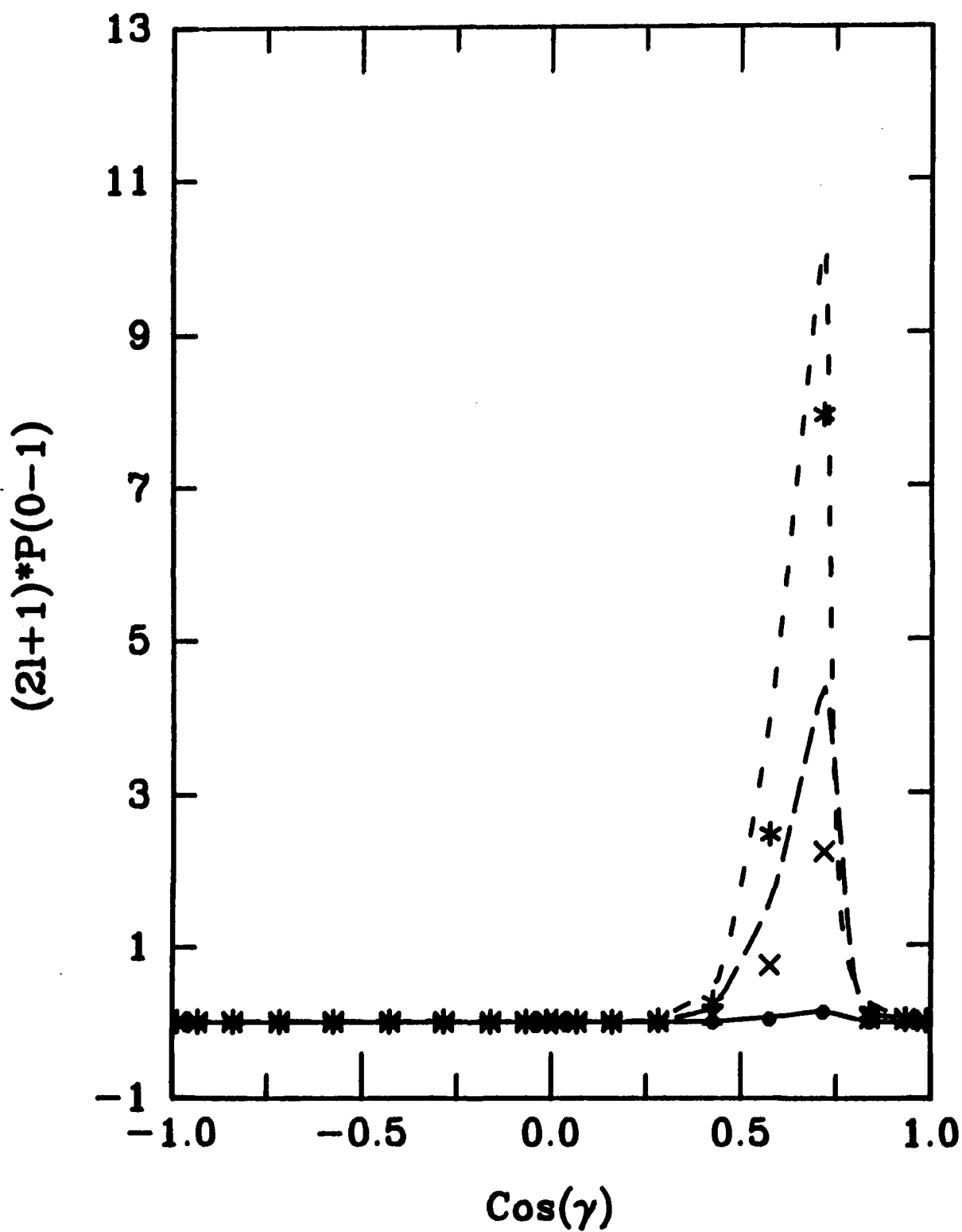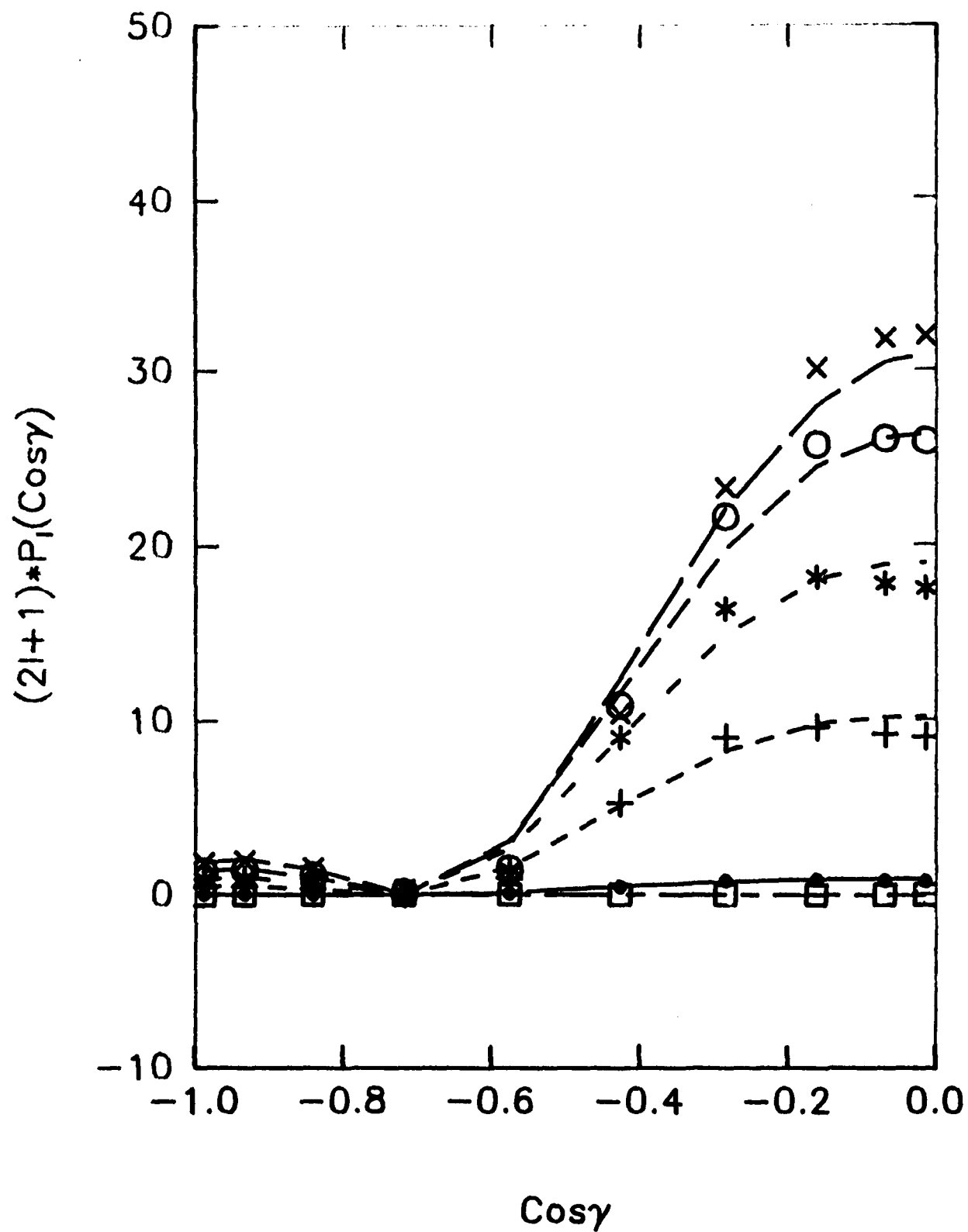
FIGURE 2b

Na+H2 RSVE(curve) vs. QIOS(point) I=0,5,10,15,20,100; E=.075au